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Water-soluble polymers from norbornene monomers.

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WATER-SOLUBLE POLYMERS FROM NORBORNENE MONOMERS

A Dissertation Presented

by

STERLING F. ALFRED

Submitted to the Graduate School of the
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Polymer Science and Engineering

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Gregory Tew, Chair

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DEDICATION

To my parents Kenrick, Vernice and Cheryl.

My brothers and sister, Seymore, Sherwin, Sheron, Tricia

and my uncle and aunt, Carl and Elberita.

ACKNOWLEDGEMENTS

This work is a culmination of years of love, dedication, hard work, and perseverance and patience, from my family, close friends, colleagues and associates. I would first like to thank my father, Kenrick, who sacrificed so much of himself to raise my brothers and myself. He is without a doubt the hardest working man I know. He started the fire of interest in the sciences with the numerous books and encyclopedias that he gave me. I thank you so much and I love you so much more than words can express. I thank my mother, Cheryl for her patience raising a stubborn boy to a compliant yet strong willed young man. I love you mom.

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Finally I would like to thank the most important person in my life, my Lord and Savior Jesus Christ who has given me a measure of intelligence and perseverance to accomplish my dreams with his help. He began this journey with me even before I was aware of his presence and he continues to guide and direct me now. Everyday I'm reminded about how wonderful a creator He is and how much he cares for each of us. Above all else his love for me knows no bounds and I want to thank Him with all my love. Thank you Lord Jesus.

ABSTRACT

WATER-SOLUBLE POLYMERS FROM NORBORNENE MONOMERS

MAY 2008

STERLING ALFRED, B.S., HOWARD UNIVERSITY

M.S., UNIVERSITY OF MASSACHUSETTS AMHERST

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Gregory Tew

Norbornene anhydride precursors were functionalized with hydrophilic moieties to yield water soluble monomers which were then polymerized without protecting groups. Homopolymer synthesis was accomplished with excellent control over molecular weight and polydispersity using Grubbs' 3rd generation catalyst at ambient temperature and pressure. Molecular weights ranged from 3 to 76 kDa with polydispersity indexes varied from 1.05 to 1.15. Copolymers were made by sequential addition of two functionalized norbornene anhydrides monomers to produce Double Hydrophilic Block Copolymers (DHBCs). All polymers were demonstrated to exist in solution as single solvated chains by dynamic and static light scattering experiments. Superabsorbent gels were prepared from carboxylic acid, amine and hydroxyl functionalized norbornene monomers. Swelling ratios for these gels were studied as a function of crosslink density and aqueous solution pH.

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CHAPTER 1

INTRODUCTION

Background

Water soluble polymers (WSP) can be classified as macromolecules that have a high affinity for water and as a result dissolve in aqueous media as single solvated chains, aggregated structures, micelles, or vesicles. Water soluble polymers can be divided into three categories according to their origin: natural, modified natural (semi-synthetic), and synthetic. The natural water soluble polymers include polysaccharides such as starch, tree exudates gums, (e.g. karaya), seed gums, (guar and carob), algal extractives (alginates), microbial gums (xanthan) and proteins such as albumin, casein, and gelatin. Modified natural WSP consists of cellulose ethers and starch derivatives (starch acetates, hydroxyethylstarch)[1].

Synthetic WSP may be nonionic, i.e. they possess non-charged groups. Polymers in this group include poly (acrylamide), poly (ethylene oxide) (PEO), and poly (vinyl alcohol). Examples of synthetic ionic WSP include poly (acrylic acid), poly (styrene sulphonate), poly (4-vinyl pyridine) and poly (vinylamine). These polyelectrolytes can develop significant charge when dissolved in a solvent of high dielectric constant. In general, for a polymer to be water soluble it must possess either polar or ionizable groups (e.g. -C=O, -OH, $-NH_2$, $-CONH_2$, $-CO_2H$, $-SO_3H$).

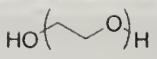
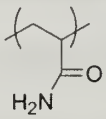
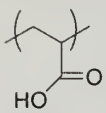
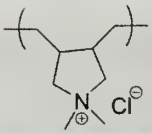
WSP have been the subject of increasing research in both academic and industrial laboratories and they represent an estimated world market of US $ 6 billion per year[2]. Most of the applications of WSP arise from their properties in solution, and especially from their abilities to: (1) modify the rheological properties of an aqueous solution and (2) to adsorb onto particles or surfaces[3, 4]. These rheological properties are a direct result of the interaction of the polymer backbone or side groups with water molecules. In most cases these interactions are: hydrogen bonding for nonionic and ionic WSPs and electrostatic interactions between charged side or backbone groups and water molecules.

Products as diverse as fracturing fluids for oil and gas production, lubricants, detergents and foodstuffs incorporate WSP to control viscosity. Polymer molecules increase viscosity as a result of their hydrodynamic volume, and viscosity may be further enhanced through intermolecular association. WSP may adsorb onto surfaces and thereby block sites at which unwanted substances could crystallize (applications include water treatment and plaque reduction). Additionally, adsorption of a polymer onto the surface of a dispersed particle may have either of two effects depending on the nature of the polymer and the conditions: (1) stabilization such that association and settling of the particles is inhibited, (e.g. in paints, cosmetics, detergents, pharmaceuticals and foods) or (2) flocculation, in which the particles are made to interact so as to be more easily separated from the surrounding medium (use in water treatment, mineral processing, and paper making)[5].

The preceding discussion highlights the important properties and applications of ionic and nonionic water soluble homopolymers. Synthetic water-soluble copolymers represent another class of WSP. In most instances the polymer is a random or block copolymer in which one monomer is hydrophilic and the other hydrophobic although in some cases both monomers can be hydrophilic (e.g. double-hydrophilic block copolymers of poly (ethylene oxide) and poly (acrylic acid) [6, 7]. These water soluble copolymers may find new applications in medicine as drug delivery agents where the hydrophobic block (core) provides encapsulation of the drug, and the hydrophilic block (corona) facilitates water solubility[8].

Crosslinked (physical or chemical) WSP comprising of either homopolymers or random copolymers may swell to form hydrogels which typically absorb 30% or more of their weight of water. Hydrogels have found uses in the controlled delivery of drugs, agrochemicals and biocompatible materials such as contact lenses. Crosslinked WSPs that absorb many times their weight are termed superabsorbent polymers and are used in personal care products (diapers and adult hygiene products), seed coating to increase germination rates, and root coatings to increase water availability[9].

Table 1.1. Commonly Used Water-Soluble Polymers.

Water-Soluble Polymer	Application	Synthetic route
PEO 	Drug delivery, laxatives, skin creams and lubricants	Ring opening polymerization of ethylene oxide
Poly(acrylamide) 	Flocculation of aqueous suspensions	Free radical polymerization in water
Poly(vinyl alcohol) 	Adhesive and thickener material in latex paints, fiber reinforcement in concrete, used in eye drops as a lubricant	Hydrolysis of poly(vinyl acetate)
Poly(acrylic acid) 	Superabsorbent polymer, coatings and adhesives	Free radical polymerization of acrylic acid or hydrolysis of polyalkyl acrylates
Poly(dimethyldiallyl ammonium chloride) 	Coagulant aid for potable water treatment	Free radical polymerization

Goals and Motivation

Table 1.1 lists some commonly used water-soluble polymers and some of their applications along with synthetic routes to obtain these polymers. In all of the above cases, the synthesis is achieved by either free radical or anionic ring opening polymerization of a suitable monomer. A glaring omission to achieve WSP is the use of ring opening metathesis polymerization (ROMP) of strained cyclic monomers, in particular norbornene monomers. Although there is vast literature on water soluble polymers made from vinyl monomers using free radical techniques[10-18], the amount of research on WSPs from norbornene monomers is

limited. In an effort to catalog the most relevant examples of WSP made by ROMP, the following discussion aims to place examples into categories according to figure 1.1.

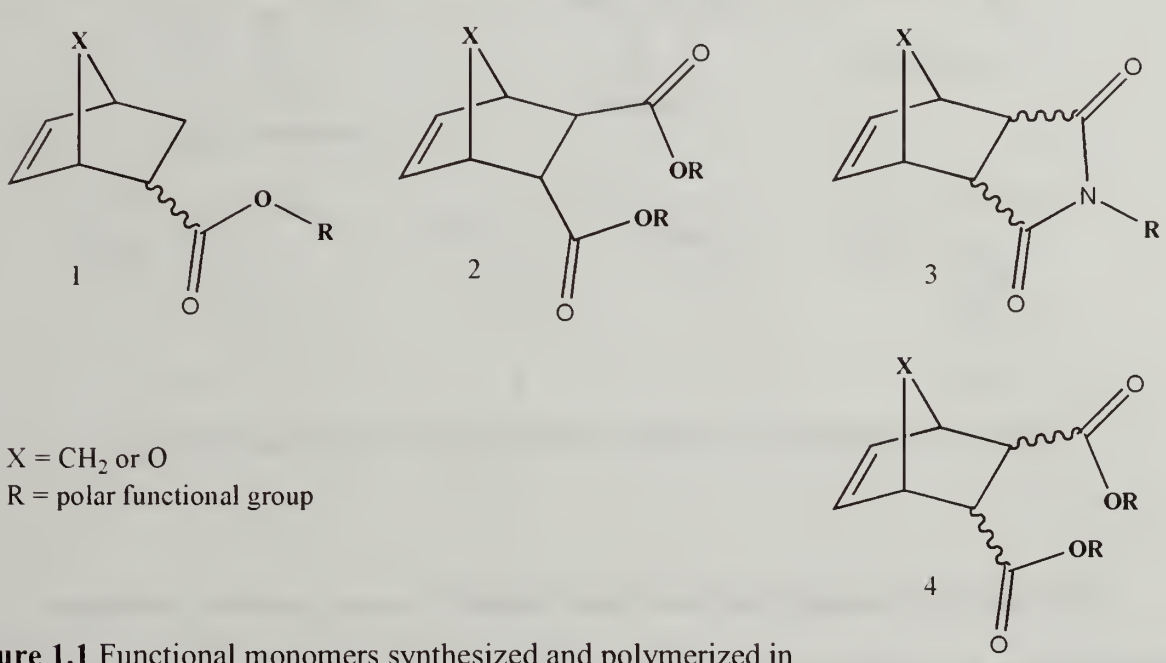


Figure 1.1 Functional monomers synthesized and polymerized in the literature.

Category 1 contains mono functional monomers that are either *endo* or *exo*. Category 2 entails di-functional monomers where if x is oxygen then the monomer is the *exo* isomer, and if x is methylene then monomer can be either *endo* or *exo*. The third group covers maleimide monomers, and category 4 list examples involving racemic norbornenes and block copolymers.

Monofunctional Norbornenes

Schrock and coworkers synthesized sugar-derivatized norbornene monomers and polymerized them using Schrock's catalyst (figure 1.2) to obtain water-soluble homopolymers and multiblock copolymers after removal of the protecting groups with trifluoroacetic acid[19]. Figure 1.2 shows the monomers and catalyst used by Schrock and coworkers. These polymers were obtained in good yield (> 90%), with molecular weights in the range of 7-112 kDa with polydispersity indices (PDI) between 1.02 and 1.25.

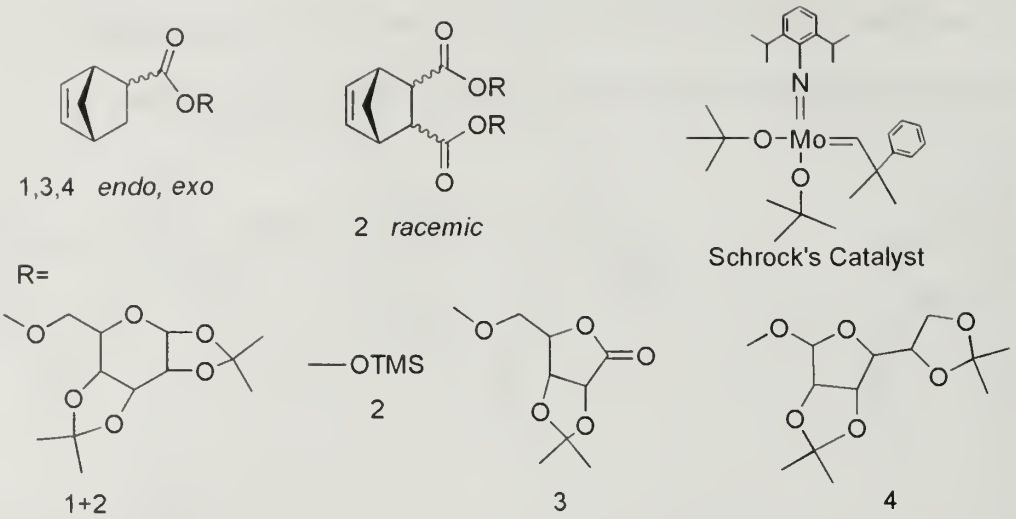
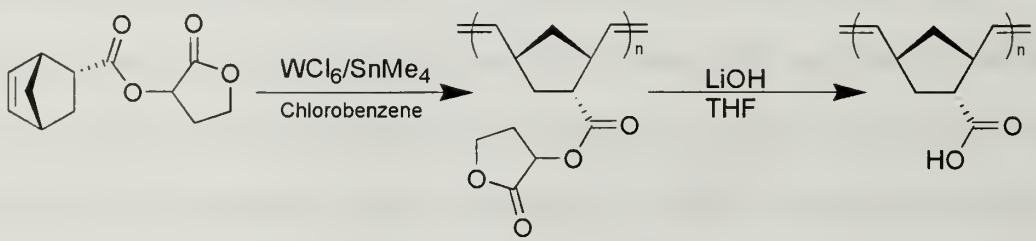


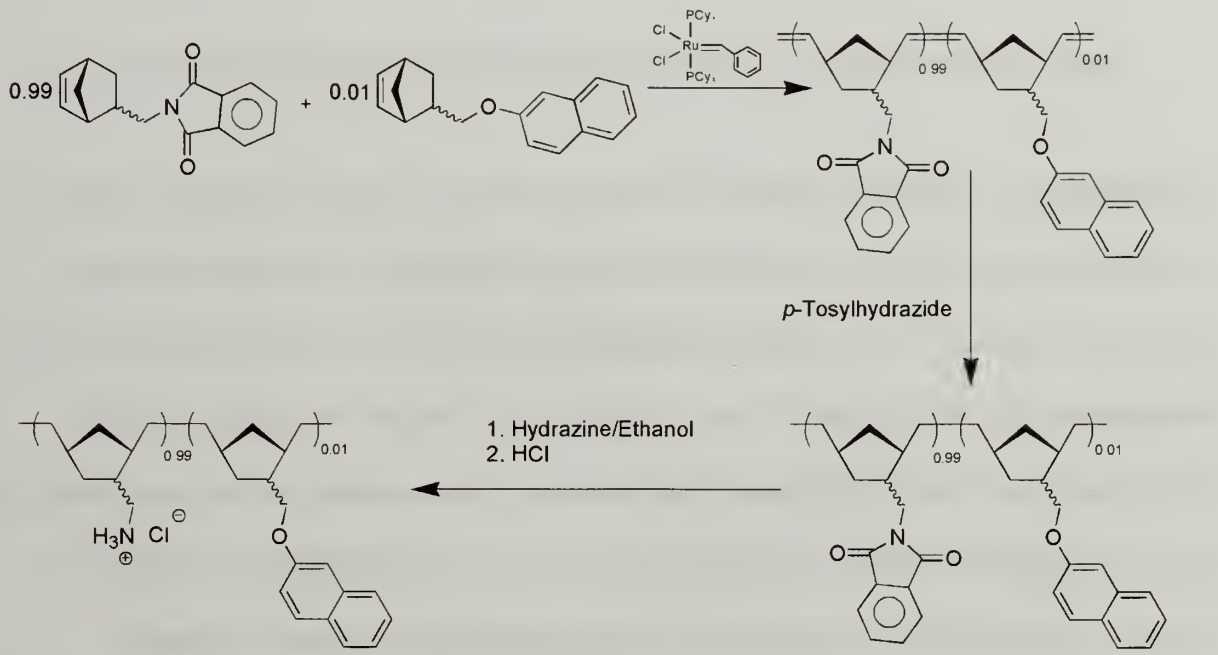
Figure 1.2 Monomers and catalyst synthesized by Schrock and coworkers.

Reyx and coworkers polymerized an endo isomer of an ester protected norbornene anhydride using Tungsten hexachloride and tetra methyl Tin as catalyst[20]. The catalyst system was freshly prepared under nitrogen in a dry-box and polymerizations were performed under dry argon in a flask fitted with a reflux condenser. WCl_6 was dissolved in chlorobenzene by stirring for 4 hours at room temperature prior to the addition of Sn $(CH_3)_4$. After addition of this solution to monomer dissolved in hot chlorobenzene the polymerization was allowed to continue for 18 hours. Hydrolysis of the resulting polymers using lithium hydroxide produced the WSP. These polymers were obtained in 87 % yield with a MW of 16 kDa reported. Scheme 1.1 outlines their synthetic approach.



Scheme 1.1 Synthetic scheme used by Reyx and coworkers.

In the preceding text, researchers achieved water solubility using carboxylic acid-functionalized and sugar-functionalized monomers. Liaw and coworkers synthesized amine-protected norbornenes from which they obtained WSP[21]. They copolymerized these amine-containing monomers with naphthalene-functionalized norbornenes using Grubbs' 1st generation catalyst (G1). They obtained a polymer with MW and PDI of 506 kDa and 1.18, respectively. Water solubility was then achieved by first deprotecting the amine using hydrazine followed by the addition of hydrochloric acid to produce the protonated amine. Liaw's monomers and synthetic scheme are shown in scheme 1.2.



Scheme 1.2 Synthetic scheme showing Liaw's WSP.

Nomura and coworkers functionalized norbornene precursors with acetyl protected sugars[22], an approach similar to that of Schrock. In this work both Schrock's and Grubbs' 1st and 2nd generation catalysts (G2) were used. Polymers synthesized using Schrock's catalysts were

reported to have MW between 9-15 kDa and PDIs between 1.11 and 1.19. An average yield of 90% was obtained. For polymers made using G1, MW and PDIs ranged from 4-15 kDa and 1.07-1.16. Surprisingly, broad PDIs were obtained when G2 was used; 1.63-1.86. MW for those samples were higher than for the previous two batches ranging from 32-43 kDa, with yields >92% reported. Figure 1.3 shows the monomers polymerized by Nomura.

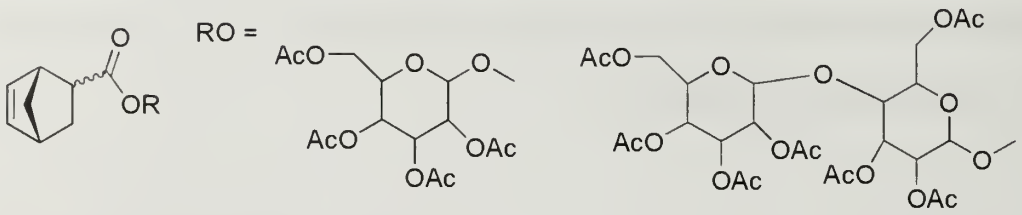
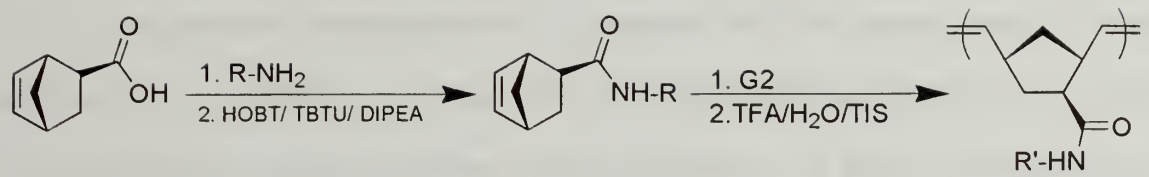


Figure 1.3 Monomers Synthesized and polymerized by Nomura and coworkers.

In a more recent presentation (May 2007) Setton and coworkers attached peptide residues (C-terminus protected with Boc and *t*-Butyl) to norbornene precursors and polymerized these monomers using G2[23]. The resulting oligopeptides had monomer to catalyst ratios of 5 and 12 corresponding to MW of 5 and 12 kDa. TLC was used to monitor the reaction and full conversions were noted in both cases. The structures of the monomers and polymers used in this study are shown in scheme 1.3. Dynamic Light Scattering experiments were performed on aqueous solutions of the 5 kDa sample to investigate the particle size as a function of temperature. For this polymer a transition temperature of 29.1°C was observed. These monomers were also synthesized by Grubbs' and coworkers[24], however, peptide sequences of five units were used in that study. Also G1catalyst was used instead of G2.The amino acid residues in Setton's work are abbreviated as follows: V = Valine, P = Proline, G = Glycine and K = Lysine.



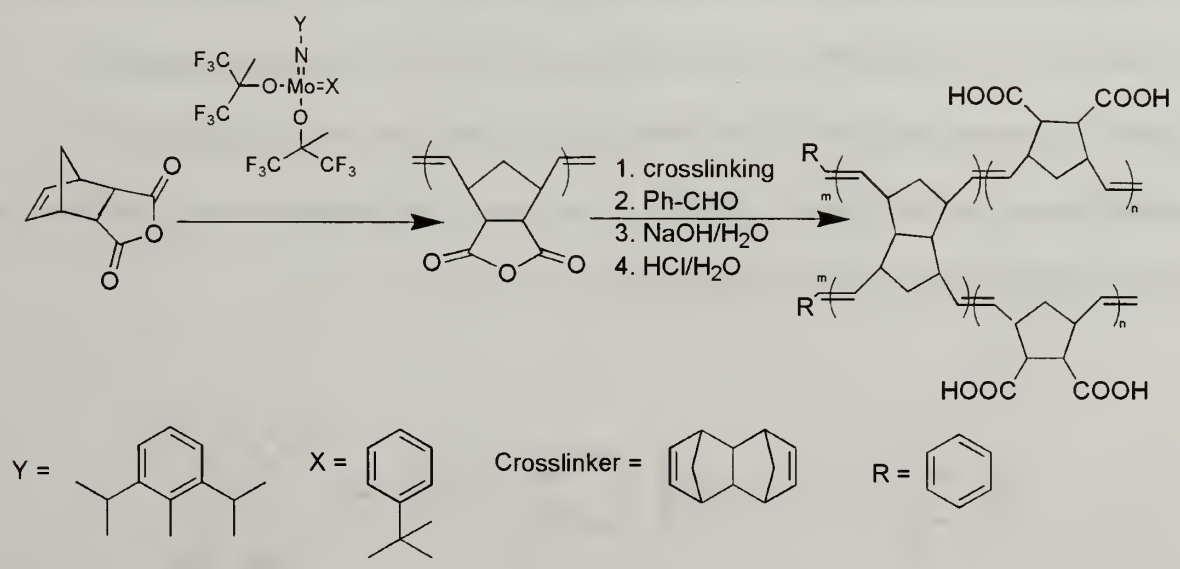
R= VPGVGVPGK(Boc)G(tBu)

R'= VPGVGVPGKG

Scheme 1.3 Synthetic scheme showing molecules made by Setton and coworkers.

Difunctional Norbornenes

Buchmeiser and coworkers synthesized carboxylic acid-functionalized polymers for use in separation techniques[25]. Their synthesis entails the polymerization of *endo* norbornene anhydride using Schrock-type catalyst followed by a crosslinking reaction and subsequent hydrolysis to obtain polymers with diacid side groups. Yields were noted to be between 90-100%. Their scheme is outlined in scheme 1.4.



Scheme 1.4 Synthesis of Polyacids made by Buchmeiser and coworkers.

Masuda and coworkers polymerized bis amino acid-functionalized norbornenes using G2[26]. For *endo* isomers, MWs reported were between 15- 210 kDa with broad PDIs of 1.6-2.0 and yields between 43 and 97% noted. *Exo* monomers had MW and PDIs between 15-261 kDa and 1.6-3.1 respectively, with yields ranging from 36-98%. Monomers used in this study are shown in figure 1.4.

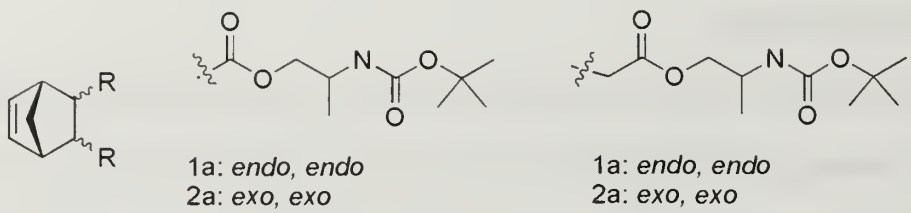
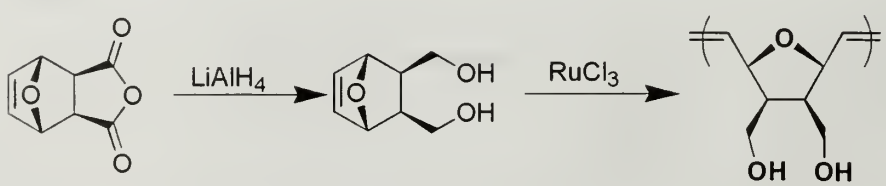


Figure 1.4 Monomers made by Masuda and coworkers.

Another monomer in this category was made by Booth and coworkers[27]. They synthesized bis hydroxyl monomers by reduction of oxanorbornene anhydride with $LiAlH_4$. This monomer was polymerized in 10, 50 and 90% v/v water in ethanol. However, the resulting product was insoluble in solvents used for GPC and NMR, which made characterization difficult. The polymer was swollen to a degree in $DMSO_6$ to provide an NMR spectrum which confirmed the structure of the polymer. This monomer is shown in scheme 1.5.



Scheme 1.5 Difunctional Monomer polymerized by Booth and coworkers.

Maleimide Norbornenes

In 2000, Grubbs and coworkers synthesized several water soluble monomers. These monomers were polymerized in water using water soluble ruthenium catalysts[28, 29]. Figure 1.5 shows the monomers and catalyst used by Grubbs and coworkers.

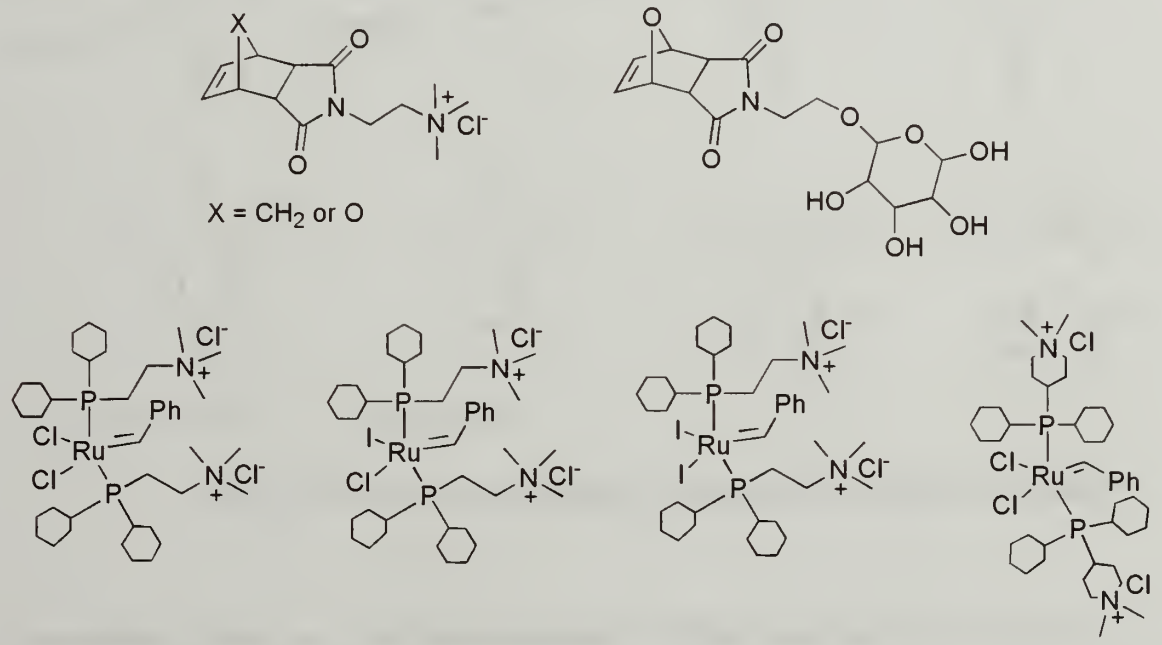


Figure 1.5 Monomers and catalyst synthesized by Grubbs and coworkers.

Polymerizations were carried out with and without the addition of deuterated hydrochloric acid (DCl). The molecular weight of one sample with DCl was reported to be 11.5kDa with a PDI of 1.24 and a yield > 95%. For polymerizations carried without DCl molecular weights were noted to be lower than expected with PDIs of 2.3 obtained. Polymer yields were in the range 45-60%. More recently, Tew and coworkers synthesized amphiphilic homopolyers[30, 31]. These polymers had molecular weights between 2-31.1kDa with PDIs ranging from 1.08 to 1.3 with obtained yields between 85-95%. Hydrophobicity of these polymers was tailored by modification of the

backbone, while polyelectrolyte character was tuned by modification of the side groups. The monomers and polymers synthesized in Tew's work are shown in figure 1.6.

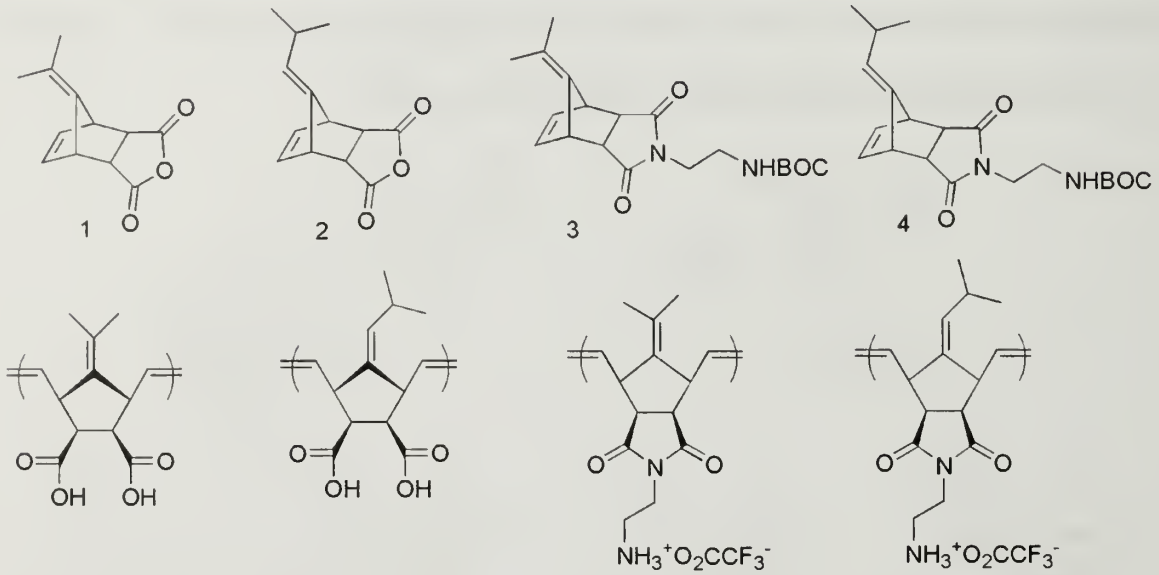


Figure 1.6 Monomers and polymers synthesized by Tew and coworkers.

Lowe and coworkers used Grubbs' 1st generation catalyst to polymerize quarternized oxanorbornene monomers[32]. These polymerizations were carried out in a novel trifluoroethanol / methylene chloride solvent mixture. Polymer MW ranged from 9-29 kDa while PDIs were between 1.02-1.24. All yields were reported > 86% as determined by NMR. Lowe's monomers are shown in figure 1.7.

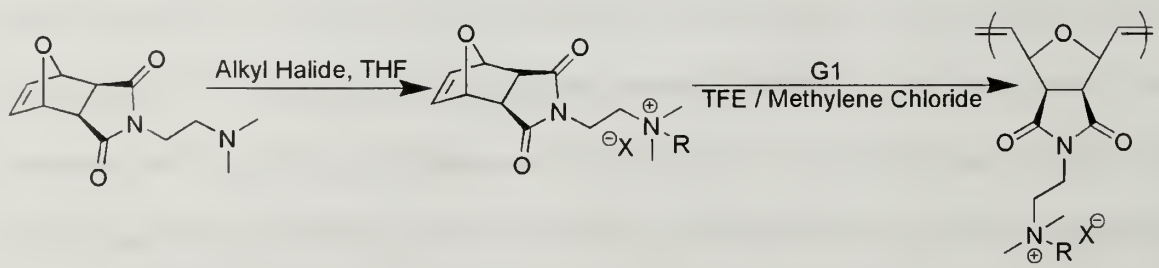
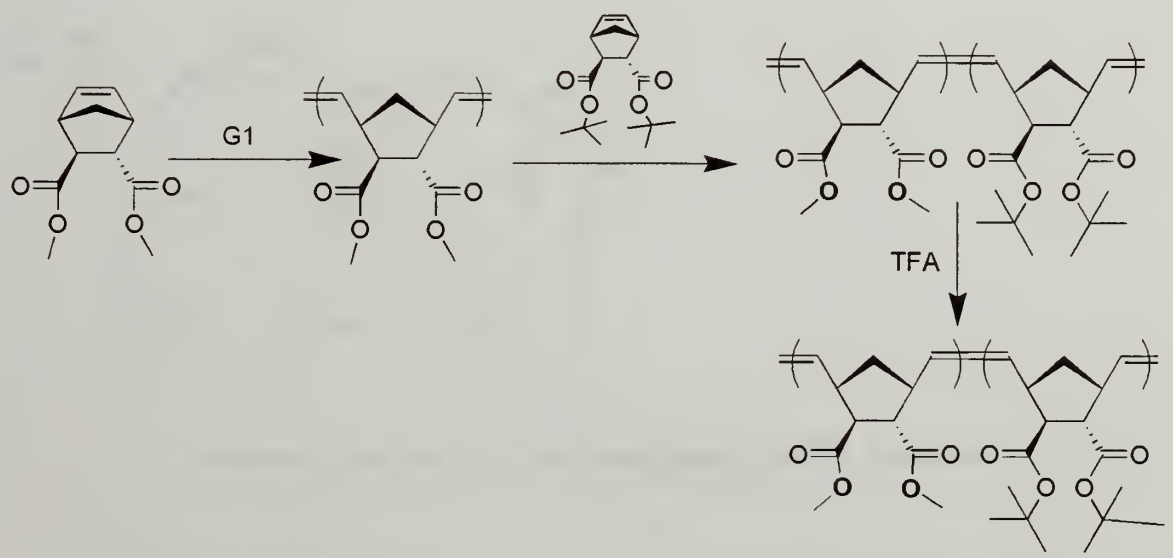


Figure 1.7 Monomers synthesized by Lowe and coworkers.

Racemic Norbornenes and Block Copolymers

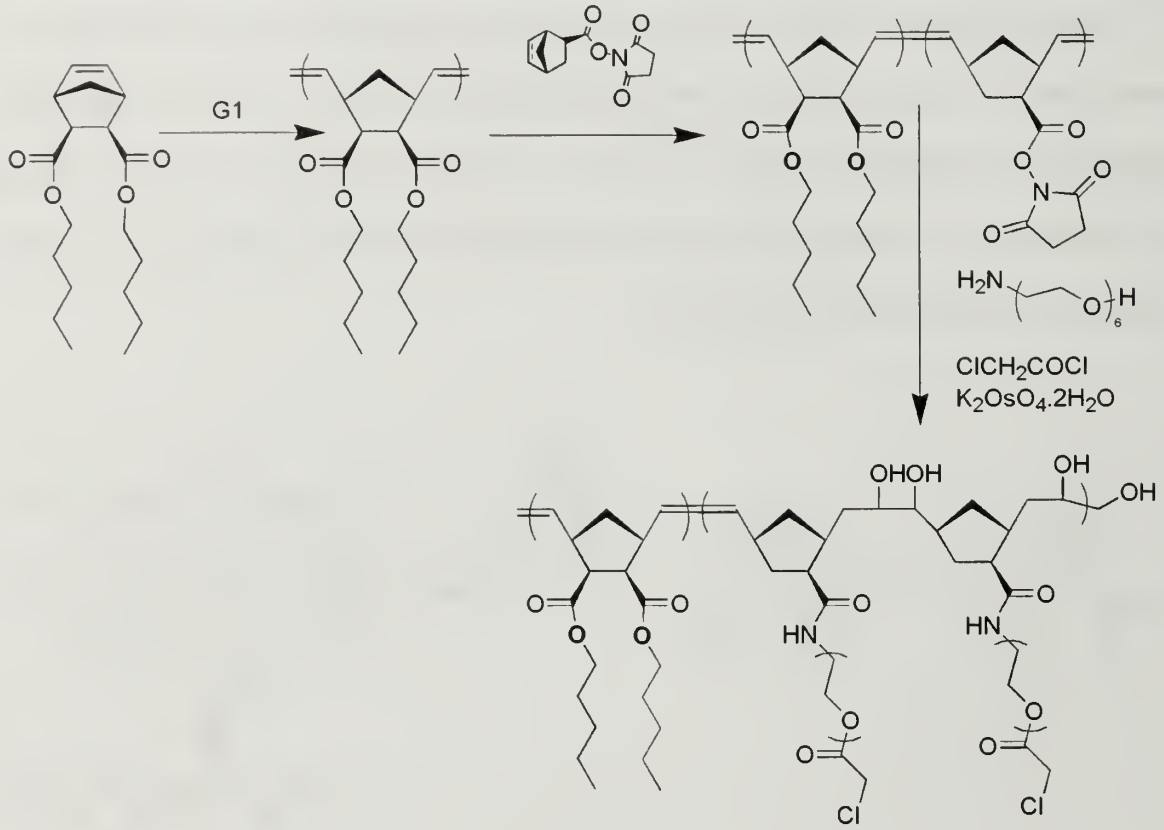
Trimmel and coworkers synthesized amphiphilic block copolymer containing racemic norbornene monomers. ROMP was accomplished using G1, with MWs of block copolymers ranging from 13-55 kDa and narrow PDIs reported between 1.07 and 1.15. These amphiphilic polymers were studied using, DLS to determine the hydrodynamic radius of the formed micelles, and small angle x-ray scattering to determine the aggregation number and shape of the micelles. Trimmel's synthesis is shown in scheme 1.6.



Scheme 1.6 Block copolymers made by Trimmel and coworkers.

Kane and coworkers prepared amphiphilic block copolymers using G2 as ROMP catalyst and post-polymerization funtionalization to introduce water soluble moieties. PDIs were all reported to be either 1.22 or 1.23. These polymers self-assembled in water to form nanoparticles with sizes ranging from 35-86nm. These nanoparticles were then biofunctionalized with a

thiolated peptide in aqueous media, with proposed applications as inhibitors and antimicrobial polymers[33]. Kane's synthetic scheme is shown in scheme 1.7.



Scheme 1.7 Block copolymers made by Kane and coworkers.

Work presented thus far provides a good foundation for the polymerization of water soluble norbornenes. The question arises as to which pathway should be taken to synthesize WSPs. On one hand, polymerizations can be carried out in water, a green solvent which is non-toxic. By this pathway water soluble catalyst will have to be used as demonstrated by Grubbs. This presents a few problems most notably is the need to use hydrochloric acid as an additive to minimize decomposition of the catalyst by hydroxide ions and ensure controlled polymerizations. Also isolation of the polymers from aqueous solution may be problematic.

Additionally, the catalysts used by Grubbs are not easily made and they are reported to have short shelf lives. Furthermore, well defined polymers were not obtained using these polymerization systems, the lowest PDIs obtained were 1.24. Although, this can be considered controlled further monomer addition to synthesize block copolymers may prove difficult. The alternative approach to synthesize water soluble polymers involves the synthesis of appropriate monomers in organic solvents. The major concern in this approach is the tolerance of the catalyst used to functional groups on the monomers. Tew, Liaw and Schrock employed this method. These research groups used protected monomers for their polymer synthesis to circumvent catalyst poisoning. Liaw used an imide as a protecting group for his polymers. After polymerization, WSP were obtained by reaction of these polymers with hydrazine followed by protonation. Schrock employed monomers functionalized with acetal protected sugars. WSP were then obtained after deprotection of the acetal groups with trifluoroacetic acid (TFA). Tew polymerized an anhydride followed by dissolution in sodium hydroxide solution to obtain polymers containing bis carboxylate functional groups. Cationic polymers were obtained by first polymerizing Boc protected amine monomers followed by removal of the Boc group using TFA. Between these two routes, the approach which involves polymerization in an organic solvent is more attractive as the monomers employed will be soluble in a variety of solvents, and modern ROMP catalysts, Grubbs' 3rd generation in particular, are stable at room temperature over an extended period of time. Grubbs' 3rd generation catalyst is also much more tolerant to a wide variety of functional groups. This provides the advantage that monomers functionalized with amines, carboxylic acid or hydroxyl groups can be polymerized directly. Furthermore, the resulting polymers can be easily isolated and purified from organic solvents.

Strategy

The preceding discussion outlines a solid foundation for further advancement in the area of water soluble polymers from norbornene monomers. First, norbornene monomers are easily synthesized and can be tailored according to the desired functionality. These monomers are amendable to one or two side groups, with asymmetric placement of functional groups possible. Second, ROMP, the technique of choice used to polymerize these monomers, allows for very good control over the molecular weight and polydispersity of resulting macromolecules. The catalyst employed (esp. the ruthenium-based Grubbs' catalyst) are tolerant to a wide variety of functional groups, which allows the direct polymerization of functionalized norbornene monomers. In addition, because of the living nature of the polymerization, block copolymer synthesis is possible which can facilitate the tuning of polymer properties. Furthermore, the resulting unsaturated polymer backbone offers the potential to further functionalize these polymers. Also, hydrogenation of the vinyl groups on the backbone increases the flexibility of these polymers which can influence the physical and mechanical properties of the resulting WSP. The unsaturated backbone also provides a route by which polymer degradation can be achieved. Coughlin and workers looked at the acyclic diene metathesis depolymerization of styrene-butadiene and styrene-isoprene ABA triblock copolymers with metal-carbene complexes[34]. In particular, Grubbs' 2nd generation catalyst was shown to be effective at depolymerizing styrene-butadiene polymers after 20 hours at 4 psig of ethylene at 20°C. Finally, polymerizations can be carried out in either aqueous or organic solutions. With such versatile techniques available to polymer chemists, one would expect an explosion in the area of synthetic WSP made from norbornene monomers. This unfortunately is not the case. One can speculate that one reason for the lack of norbornene containing WSP is that on an industrial scale, free radical polymerizations

are more cost effective. Also the synthetic processes, e.g. poly (acrylic acid), have been thoroughly optimized. Another drawback lending to the lack of norbornene based water soluble polymers is the need to employ protective groups for example the polymers made by Schrock[19] were synthesized as the protected sugar molecules followed by hydrolysis after polymerization. The cationic amphiphilic polymers made by Tew[31] were first polymerized as the protected amine followed by deprotection with trifluoroacetic acid. Although the protection–deprotection chemistry does not affect the utility of the resulting polymers, it makes them more costly. The following thesis work is thus motivated by the need to obtain water-soluble polymers from functionalized norbornene monomers without the need for protection-deprotection chemistry. Using Grubbs' catalyst and ROMP will enable us to control the molecular weight (MW) and polydispersity of the resulting polymers. Finally, water solubility will be ascertained by the use of light scattering methods.

Olefin Metathesis History

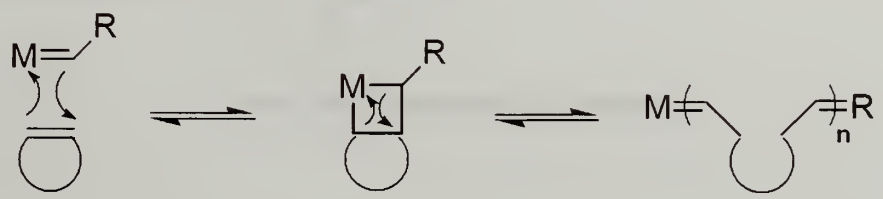
The non-catalytic disproportionation of olefins has been known since 1931, when Schneider and Frolich obtained ethene and 2-butene by heating propene at 852° C.[35] In 1964, Banks and Bailey obtained ethene and 2-butene by the disproportionation of propene in the presence of heterogeneous catalytic systems consisting of alumina-supported molybdenum hexacarbonyl, tungsten hexacarbonyl or molybdenum oxide[36]. In 1967, Calderon, Chen and Scott carried out the disproportionation of 2-pentene in the homogenous phase for the first time and coined the term metathesis[37]. This catalytic system was composed of tungsten hexachloride, ethanol and ethyl-aluminum dichloride. Also in 1967, Calderon et al applied the metathesis to cyclo-olefins to produce polymers with unsaturation along the backbone[38]. Other research groups

joined the proliferation of metathesis by expanding the range of monomers and catalytic systems. Pennella, Banks and Bailey carried out metathesis on acetylenes[39], Heckelsberg, Banks and Bailey reported the metathesis of dienes[40], and various research groups polymerized olefins and cyclic olefins bearing different functional groups[41-43].

The reaction kinetics and mechanism of the olefin metathesis has been studied since 1967. In the disproportionation of 1-butene with heterogeneous catalyst, Bradshaw, Howman and Turner obtained results which suggested a reaction mechanism through a four –centered cyclobutane intermediate[44]. At the same, Calderon et al also proposed a similar mechanism for metathesis and ring opening polymerization in the homogenous phase [45, 46]. At the time the exact nature of the active species was not well known but Chauvin et al performed tungsten-catalyzed cross metathesis reactions between cyclopentene and 2-pentene, the resulting products led them to propose a transition metal-carbene complex as the catalytically active species[47]. This finding was subsequently confirmed by independent studies involving isotope labeling, kinetics, and single component transition metal-carbene complexes[48]. More recent advances in olefin metathesis involves the work of Osborne (Osborne 1982), who used tungsten carbene complexes in the presence of Lewis acids as a catalyst, and Schrock et al. who applied molybdenum based single-component homogenous carbene catalysts to perform ROMP on cyclic olefins and ring closing metathesis (RCM) on various unsaturated molecules[49-54]. In addition, the work of Grubbs et al. has provided the polymer chemist with several generations of catalyst to achieve living polymerizations of functionalized cyclic olefins, in particular norbornene and its derivatives[55-61].

Ring Opening Metathesis Polymerization (ROMP)

ROMP is a very versatile polymerization technique for strained cyclic monomers. It relies on a transition metal-based catalyst (usually ruthenium, molybdenum or tungsten) to achieve fast reaction rates. Ring opening polymerizations are thermodynamically favored for 3-,4-,8-, and larger-membered ring compounds and will proceed if a mechanism is available [62]. For molecules containing 5-, 6-, and 7- membered rings the situation is critical as these rings are less strained and hence do not readily polymerize. The change in free energy (ΔG) for the polymerization process may be sensitive to a number of physical factors such as monomer concentration, temperature and pressure. Chemical factors such as the nature of the substituent and relative position in the ring also play a role. For bicyclic molecules, ΔG for the ring opening of a particular ring will be more negative as a result of the increased strain energy in the monomer.

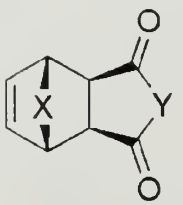


Scheme 1.8. Ring opening metathesis of norbornene with metal-based catalyst.

Scheme 1.8 illustrates the general reaction that occurs between a metal based catalyst and a cyclic monomer to produce polymer chains. The intermediate structure in scheme 1.1 is the transition metal-carbene complex that was proposed by Chauvin as the catalytically active species in ROMP[47]. This mechanism is accepted today as the predominate pathway for metathesis reactions. Polymerizations can be done at room temperature and high molecular weight polymers can be obtained within minutes[63]. Tungsten- or molybdenum-based catalysts

have very high polymerization rates, thus permitting the polymerization of many sterically hindered olefins. However, they are very sensitive to oxygen and not very tolerant to protic or polar functional groups including alcohols, acids, and aldehydes. Ruthenium based catalysts (Grubbs' catalysts) have comparable reaction rates to Schrock type catalysts (molybdenum based) but they have added advantages in that they are not highly sensitive to oxygen and are very tolerable to a wide range of functional groups[64]. Grubbs' catalyst is also amenable to living polymerizations where control over MW, polydispersity, end-group control and block copolymer synthesis are desired.

Norbornene Anhydride



X = Carbon or Oxygen
Y= Oxygen or Nitrogen

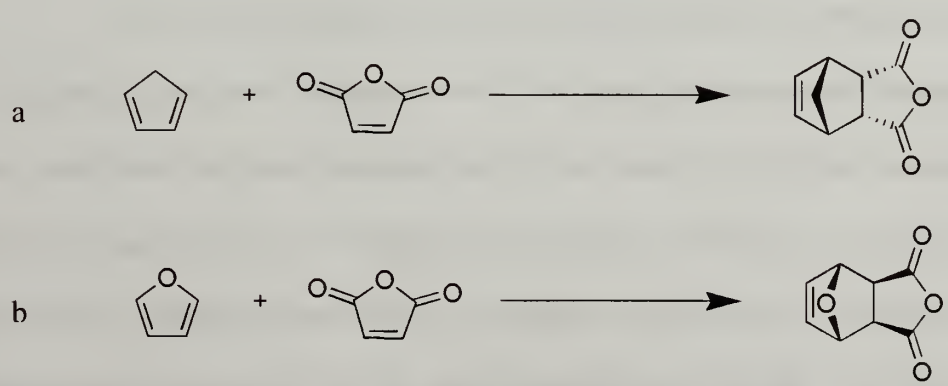
Figure 1.8 Norbornene Anhydride

The norbornene anhydride is a versatile starting precursor from which many functional monomers and tailored polymers can be made. Figure 1.8 shows the general structure of this monomer, the most widely used version being the derivative with X= carbon and Y = oxygen. The following table shows the number of substances and reactions obtained from a search in SciFinder scholar for the norbornene anhydride precursor while varying X, and Y. The search includes both the *exo* and *endo* isomers of the anhydride.

Table 1.2. Substance and reaction hits for Norbornene Anhydride precursor using SciFinder Scholar.

X	Y	SciFinder Scholar Hits Substances	SciFinder Scholar Hits Reactions
Carbon	Oxygen	869	1113
Carbon	Nitrogen	23	379
Oxygen	Oxygen	58	635
Oxygen	Nitrogen	22	113

ROMP reactions are known to occur faster for the exo isomer of norbornene anhydride and its derivatives[65]. Thus the *exo* isomer of the norbornene anhydride was chosen as the precursor for our monomer syntheses. These precursors are easily made by Diels-Alder [4 + 2] cycloaddition between a diene and an appropriate dienophile. In particular, the diene used in this work was either furan or cyclopentadiene, and the dienophile was maleic anhydride.



Scheme 1.9. Norbornene precursor synthesis using cyclopentadiene (a), and furan (b).

Scheme 1.9 shows the general scheme used to obtain norbornene anhydride precursors. It is interesting to note that cycloaddition using cyclopentadiene gives predominately *endo* product,

while furan gives exclusively *exo* adduct. These observations are believed to involve secondary orbital interactions between the *p*-orbitals on the furan oxygen and the new vinyl p-orbitals in the intermediate state. This interaction favors formation of the *exo* monomer. A theoretical study by Suarez and coworkers asserts that the *endo* intermediate formed between furan and maleic anhydride has free energy values of 21.67 and 19.26 kcal/mol in the gas phase and in acetonitrile solution respectively, these values are only 0.56 and 0.25 kcal/mol below those of the *exo* isomer. Dispersion interactions, which stabilize the endo isomer through π-π interactions and solvent effects favoring the *exo* isomer are the main factors governing the selectivity of the cycloaddition[66]. More recently, Svatos et al determined free energy profiles for the formation of both adducts [67]. These experiments show that for maleic anhydride and furan the *exo* species is more stable by approximately 11.5 kJ/mol, the energy of formation of both isomers is approximately the same. For maleic anhydride and cyclopentadiene the *exo* monomer is only slightly more stable (2kJ/mol), however, the energy barrier for formation of the *endo* intermediate is lower than the *exo* and hence the *endo* adduct is preferentially formed.

This thesis outlines the synthesis of water soluble monomers derived from functionalizing norbornene anhydride precursors. These monomers were polymerized using Grubbs' 3rd generation catalyst to produce well defined homopolymers and block copolymers with excellent control over molecular weight and PDI. Dynamic Light Scattering was used to prove that these polymers existed in aqueous solution as single solvated chains. The last chapter of this thesis details the synthesis of superabsorbent gels derived from water soluble monomers and a PEO functionalized crosslinker. The following chapter details the synthesis of WSP containing carboxylic acid functionality

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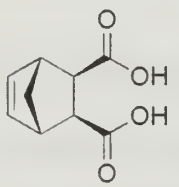
CHAPTER 2

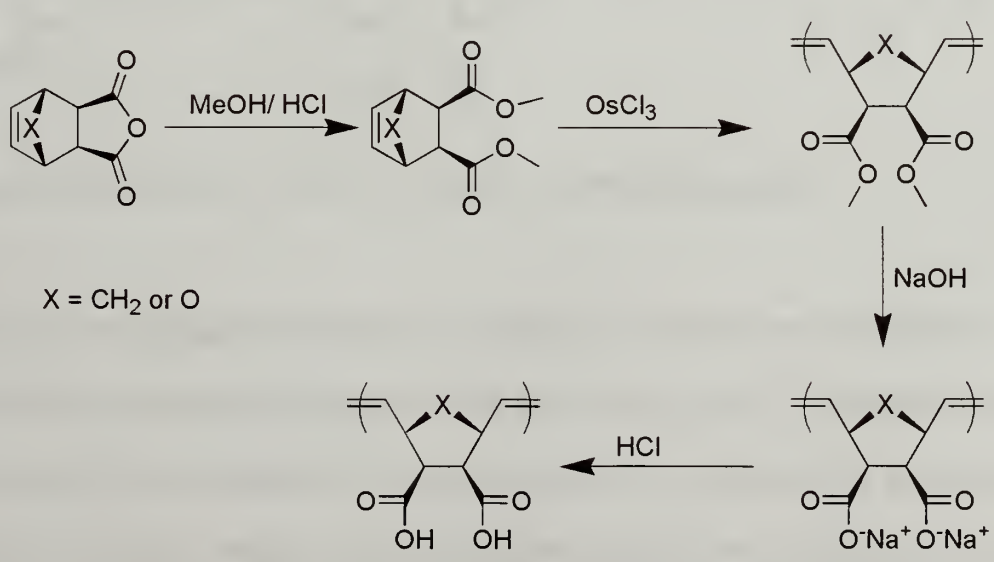
SYNTHESIS AND POLYMERIZATION OF NORB-DIACID



Introduction

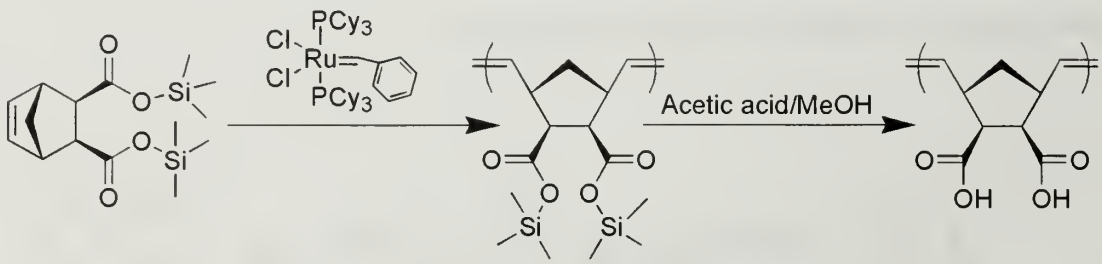
Polymers bearing carboxylic acid side groups are important in various areas of science. Water-soluble polymers containing this moiety are used as flocculants for waste purification, in the extraction of various heavy metals, in the paper industry and as superabsorbant gels after being physically or chemically crosslinked [1-3]. Polydispersity control is not a desired property for these applications as this adds extra costs to the manufacturing process, but more recently WSP bearing carboxylic acid groups are being used in drug delivery and medical applications [4-6] and as model biological systems [7]. These applications require control over both polydispersity and MW as the aforementioned applications are usually MW dependent. This requirement dictates that the synthesis of these WSP be accomplished using a controlled living polymerization technique. This process not only ensures control over the MW and polydispersity of the resulting polymers, but it also facilitates block copolymer synthesis and to a certain extent control over the end groups of the polymer. Although new metathesis catalysts allow the polymerization of a wide range of monomers, no literature is reported for the *direct* polymerization of norbornene functionalized with carboxylic acid groups.

However, there are a few examples of acid protected norbornene monomers polymerized using ROMP. One of the first examples was accomplished by Hamilton and coworkers[8] in 1995, they polymerized the dimethyl ester of *exo* norbornene anhydride using ruthenium trichloride as catalyst. The resulting polymers were hydrolyzed with sodium hydroxide to yield polymers that were reported to be water soluble. After addition of hydrochloric acid to aqueous solutions of the above polymers the free acid versions of these polymers were obtained. No GPC data was reported for these polymers. Thus information about molecular weights and polydispersity were not reported, however, proton NMR experiments show that quantitative hydrolysis of the methyl esters was accomplished. Intrinsic viscosity was reported for most of the polymers presented and yields obtained were reported between 35-51% with reaction times between 24-160 hours. The synthetic approach of Hamilton is outlined in scheme 2.1.



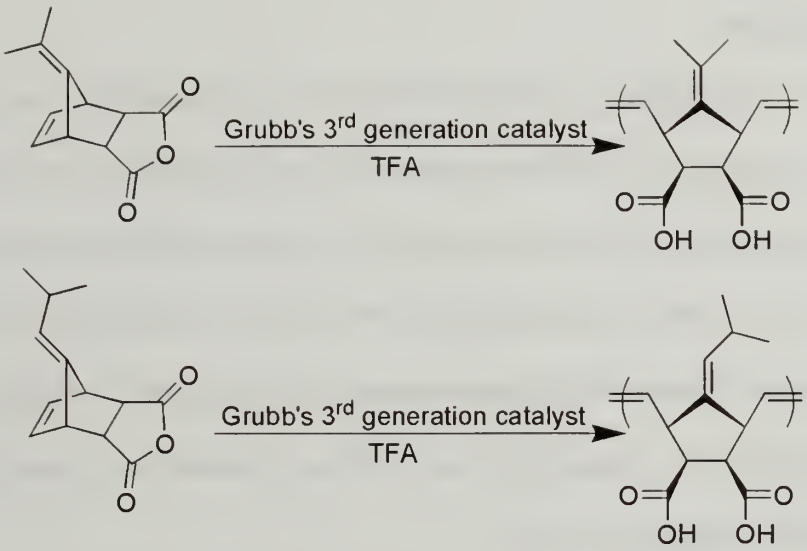
Scheme 2.1 Synthetic scheme for Hamilton's water soluble polymers.

Another example of an acid functionalized norbornene polymerized by ROMP was accomplished by Kofinas et al.[9] Kofinas polymerized the trimethylsilyl protected esters of norbornene anhydride using Grubbs 1st generation catalyst. Reaction times of 24 or 36 hours were reported for these reactions. Polymer yields were not reported. Molecular weights of 9, 18 and 27 kDa were synthesized with corresponding PDIs of 1.41, 1.28 and 1.11 obtained. The trimethylsilyl polymers were deprotected to give the free acid by dissolving the polymers in a mixture of methanol, acetic acid and water. Proton NMR was used to ascertain the deprotection reaction which was shown to be quantitative. The synthetic scheme representing the work of Kofinas et al is shown in scheme 2.2.



Scheme 2.2 Synthetic scheme for Kofinas' water soluble polymers.

More recently, Tew and coworkers, synthesized amphiphilic homopolymers using Grubbs' 3rd generation catalyst[10]. These polymers were obtained by polymerizing functionalized norbornene anhydrides for 30-60 minutes as shown in scheme 2.3. The corresponding polyacids were obtained by hydrolysis with sodium hydroxide. Molecular weights between 2.9 -19.5 kDa were obtained with PDIs between 1.14-1.63 reported. For these polymers yields between 88-90% were noted.



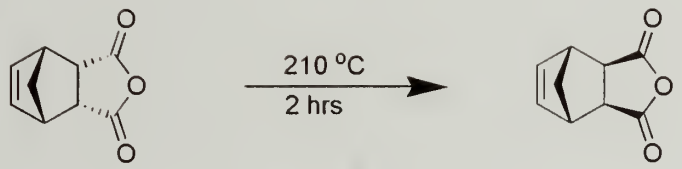
Scheme 2.3 Synthetic scheme for Tew's water-soluble polymers.

The preceding discussion shows that for norbornene anhydride monomers functionalized with protected carboxylic acid groups, polymerization can be achieved using ROMP catalysts. These polymerizations have historically been performed on acid protected monomers due to the sensitivity of the catalyst employed to acidic functionality [11]. With the advent of newer metal carbene catalyst, Grubbs 3rd Generation catalysts in particular[12], the direct polymerization of these acid functionalized norbornenes became possible. This chapter focuses on the synthesis of water-soluble polymers bearing two carboxylic acid groups per repeat unit with particular attention being paid to MW control. It will be shown that improvements have been made over the initial attempts to produce ROMP based polymers containing carboxylic acid side groups.

Experimental Section

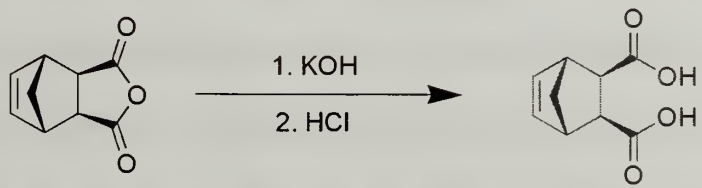
Materials. 5-norbornene-2, 3-dicarboxylic anhydride (*endo*) (99%) was obtained from TCI. Grubbs 2nd Generation Catalyst was purchased from Sigma-Aldrich and was used as received. 3-Bromopyridine (94%) was purchased from Sigma-Aldrich and used without further purification. 2, 6-Di-*tert*-butyl-4-methylphenol (99%) (BHT) was purchased from Sigma-Aldrich and used as received. (Trimethylsilyl) diazomethane (TMSDM) 2.0M in diethyl ether was bought from Sigma-Aldrich. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under nitrogen prior to use.

Synthesis of Norb-Diacid. The *exo* adduct was synthesized according to a modified procedure by Lemay [13] as shown in scheme 2.4. 100g (0.61 mol) of commercially available 5-norbornene-2, 3-dicarboxylic anhydride was placed in a 250mL Erlenmeyer flask and heated to 210°C for 2 hours under nitrogen atmosphere. After cooling to 70°C, 100 mL of toluene was added; the resulting mixture was filtered. The residue was recrystallized three times from toluene to afford 5-norbornene-2, 3-dicarboxylic anhydride (*exo*) as white crystals (15g, 15% yield). Mp 143°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (d, J= 1.2Hz, 1H), 1.66 (d, J=1.2Hz, 1H), 3.01 (s, 2H), 3.47 (s, 2H), 6.43 (d, J= 10.2Hz, 2H). ^{13}C NMR (75MHz, $CDCl_3$) δ 137.95, 71.61, 48.77, 46.87, 44.11 which agrees with known literature values.



Scheme 2.4 Isomerization of 5-norbornene-2,3-dicarboxylic anhydride.

5g (0.030mol) of *exo* 5-norbornene-2, 3-dicarboxylic anhydride was added to 50mL of water containing 4g (0.070mol) KOH. The mixture was left for 30 mins after which the solution was washed with 500mL of ethyl acetate. HCl was then added drop-wise to the aqueous solution until the diacid precipitated, this synthesis is summarized in scheme 2.5. The white solid was dried under vacuum for 24 hrs and then weighted to give 5.4g (yield 98%) of product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (d, J= 1.2Hz, 1H), 2.18 (d, J= 1.2Hz, 1H), 2.70 (s, 2H), 3.15 (s, 2H), 6.25 (s, 2H), 9.57 (br s, 1H). The ^{1}H NMR spectrum is shown in figure 2.1. ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.42, 138.05, 47.86, 45.48, 45.35. IR cm^{-1} 935, 1406, 1684, 1684. FAB-MS m/z 183 (M^+). Characterization data is in agreement with known values reported in literature.



Scheme 2.5 Synthesis of Norb-Diacid.

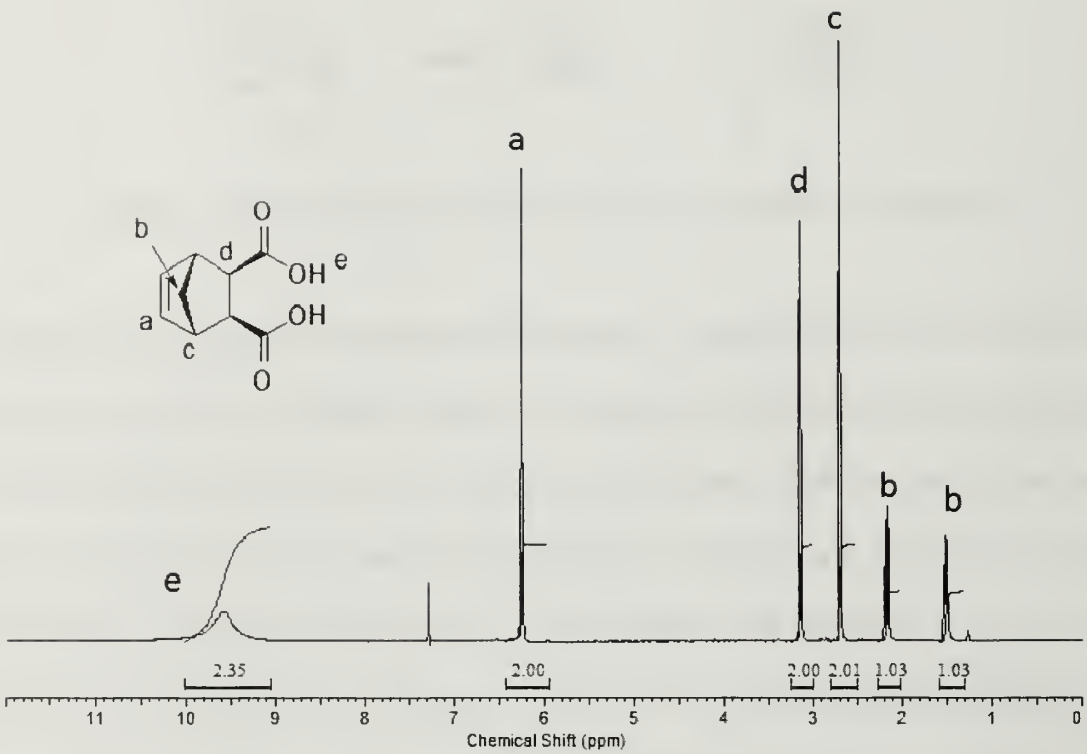
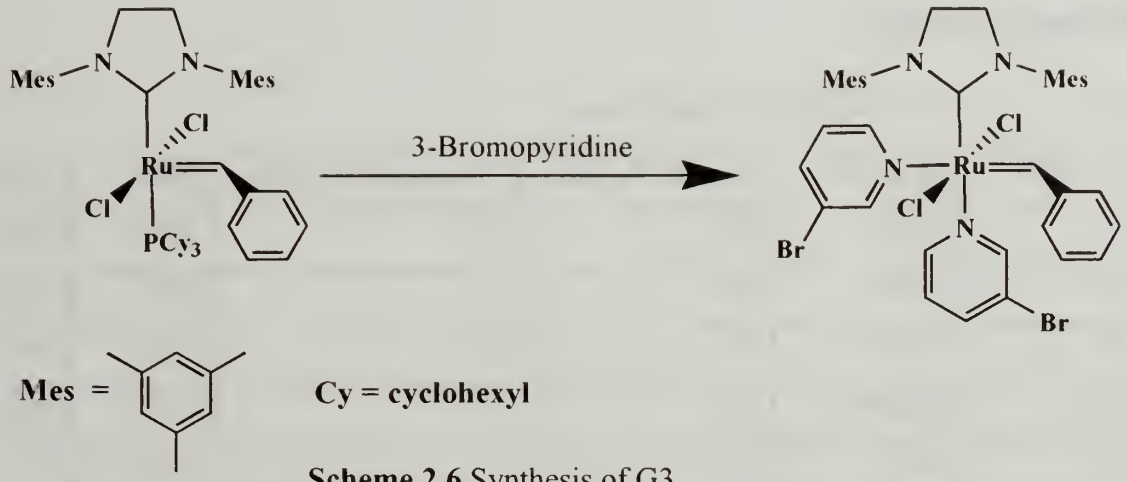


Figure 2.1 ^{1}H NMR spectrum of Norb-Diacid in $CDCl_3$.

Polymerization of Norb-Diacid. Grubbs 3rd generation (G3) catalyst was used to polymerize this monomer. G3 was made according to a published procedure [14] and the structure is shown in scheme 2.6. 200mg (23mmol) was placed in a Schlenk flask. Excess 3-bromopyridine (2mL 0.020 mol) was added and the reaction was left for 45 mins. G3 (156 mg yield = 75%) was precipitated from spectroscopic grade pentane as a bright green solid. (Scheme 2.6)



Mes =

Cy = cyclohexyl

Scheme 2.6 Synthesis of G3.

A typical polymerization was carried out as follows: 0.10 g (0.55 mmol) of Norb-Diacid and 1.3 mg (5.9 μmol) of BHT were placed in a Schlenk flask and evacuated for 10 mins. An appropriate amount of G3 (depending on desired MW) was placed in another Schlenk flask and evacuated for 10 mins. In this case 3 mg (3.3 μmol) was used. Freshly distilled THF was placed in a third Schlenk flask and degassed by 3 freeze-pump-thaw cycles. After warming to room temperature, 1 mL of this solvent was added to both monomer and catalyst. The monomer solution was then added by using a Hamilton syringe to the catalyst solution and the reaction left for 4 mins. The polymerization was quenched using 2 mL of ethyl vinyl ether. The polymer was recovered by precipitation from ether as a white solid.

Results and Discussion

Table 2.1. Polymerization data for Norb-Diacid.

[M] / molL^{-1}	[I] molL^{-1}	Target M_n /kDa	[a] Obtained M_n /kDa	PDI	Yield
0.35	0.0008	80	92	1.05	99%
0.36	0.0011	60	76	1.07	99%
0.18	0.00065	50	58	1.06	99%
0.18	0.00086	38	49	1.05	99%
0.22	0.0017	24	31	1.09	99 %

[a] *MWs obtained from GPC calibrated with linear polystyrene with THF as eluent. Polymer samples were methylated prior to injection to prevent irreversible absorption to the columns.*

The yields in table 2.1 were determined gravimetrically. Polynorb-diacid was characterized by ^{1}H NMR and GPC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (br s, 1H), 1.99 (br s, 1H), 2.75 (s, 2H), 3.20 (br s, 2H), 5.24 (s, 1H), 5.43 (s, 1H), 12.03 (br s, 2H).

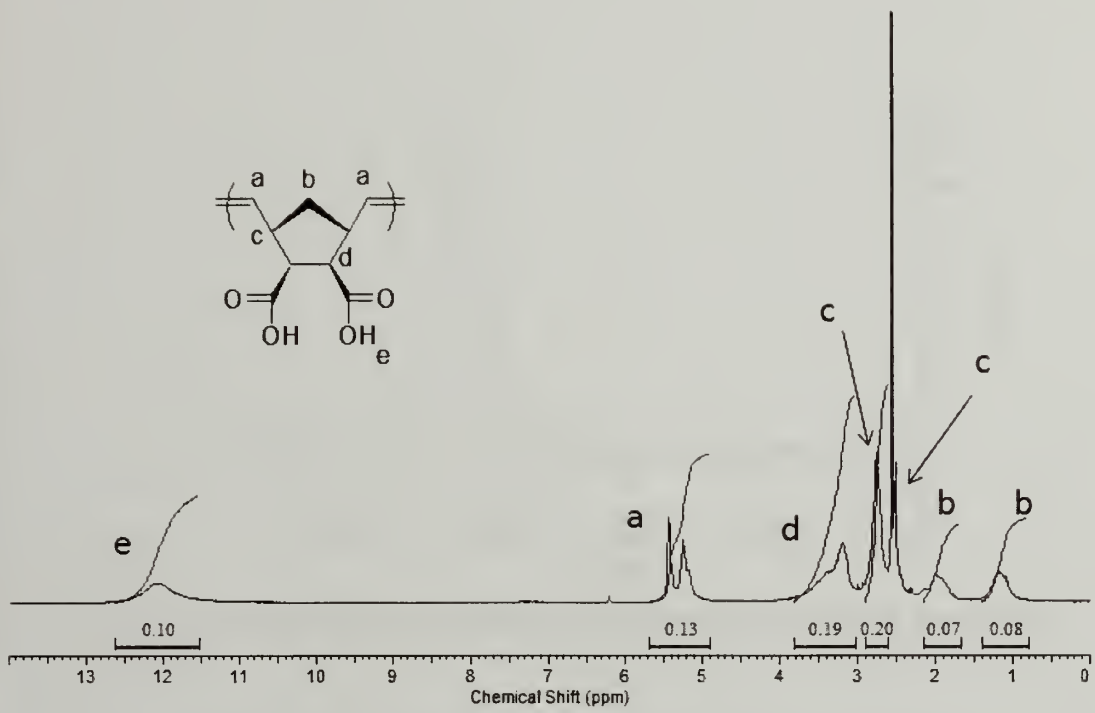


Figure 2.2 ^{1}H NMR spectrum of PolyNorb-Diacid in $DMSO_6$.

Prior to characterization by GPC, polymer samples (~20mg) were dissolved in methanol/THF (1:1) mixture. Approximately 2 mL of TMSDM was added to the solution to methylate the acid side groups. After 15 mins, the solvents were removed under vacuum and the samples placed in the GPC instrument. The obtained MWs were all in very good agreement with the target values. The difference between the targeted and obtained MW can be attributed to the non-ideal GPC standard used. Polymers obtained all had low polydispersities and were monodisperse (figure 2.3). A plot of number average molecular weight versus degree of polymerization was plotted and shown in figure 2.4. This plot provides additional evidence that the polymerization of this monomer is living. Precise kinetic studies were not performed for the polymerization of these monomers, but a rough estimate for the number of monomer units added per min for each chain was ascertained to be 30 units per min. The significance of this is that high molecular weight polymer can be made in a relatively short period of time.

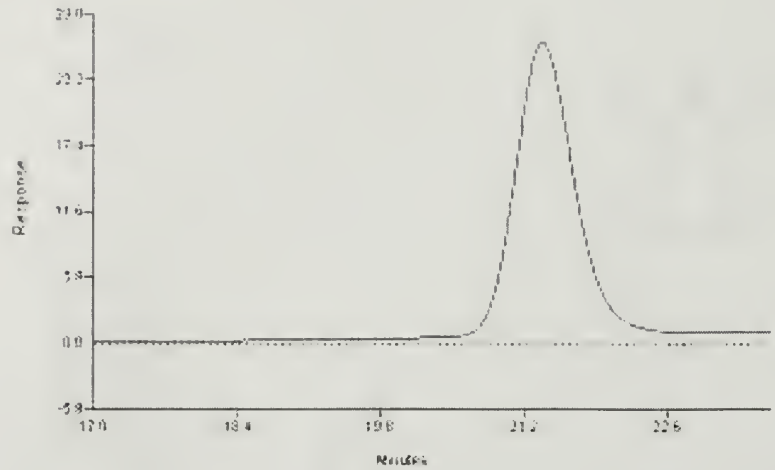


Figure 2.3 GPC trace for polynorb-diacid with M_n = 49kDa, PDI = 1.05.

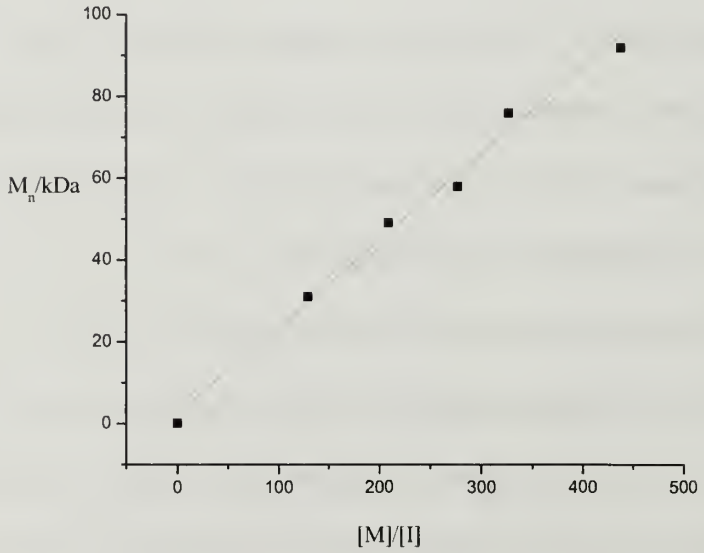


Figure 2.4 Plot of M_n vs. DP for PolyNorb-Diacid.

Previous work to synthesize water soluble polymers by ROMP provided the foundation for this present work. Kofinas, Hamilton and Tew have shown that WSPs polymers containing carboxylic acid groups with molecular weights between 2-27 kDa can be synthesized. There are

however, a few drawbacks to the techniques employed in each case. Hamilton and coworkers used ruthenium trichloride as catalyst which necessitates that synthesis be done in oxygen free environments and in aqueous solution. Also the rate of propagation using ruthenium trichloride catalyst is very slow and hence long reaction times are needed for near quantitative conversions. As a consequence of this, if initiation is slow, one of the criteria for living polymerizations will not be met and hence no control over MW or PDI will be achieved. Kofinas and coworkers used more modern catalyst (Grubbs' 1st generation) which provided faster reaction times. However, in some of their cases broad PDIs were obtained. Tew and coworkers used Grubbs' 3rd generation catalyst which facilitated the synthesis of monodisperse polymers. However, reaction times varied between 30 minutes to an hour for polymers with MW between 3-19 kDa. Additionally, for these polymers, precipitation was observed to occur before full conversion. In all of these reports the final WSP was obtained by deprotection. Also in all of these cases no aqueous solution property studies were performed to confirm the apparent dissolution of these polymers. For our system no protection of the acid groups is necessary which means that we have 100% functionality on every monomer unit in the polymer. Both monomer and polymer are fully soluble in THF and our polymers are easily obtained and purified. Furthermore, we have narrow PDIs over a range of monomer to catalyst ratios. Rate of polymerization for our monomers is very much faster than previously reported by all of the above groups. Finally, none of the aforementioned groups performed solution studies on their water soluble polymers, in chapter 6 we present Dynamic Light Scattering data used to characterize our WSPs in solution. This chapter demonstrates that we can easily synthesize and polymerize diacid functionalized monomers without protection-deprotection chemistry. Furthermore, the results obtained show that we can control the MW and polydispersity of these polymers. The control over MW and PDI

coupled with fast polymerization rates can be advantageous in various industrial applications. One can envision polymers derived from this monomer as an alternative to polyacrylic acid in superabsorbant applications, coatings and adhesives. The following chapter details the synthesis and polymerization of an amine functionalized norbornene anhydride. This synthesis represents one of the first examples of the direct polymerization of an unprotected amine using ROMP chemistry.

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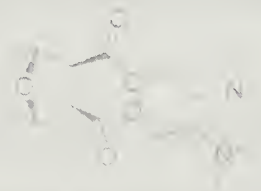
CHAPTER 3

SYNTHESIS AND POLYMERIZATION OF OXO-NORB-DIAMINE



Introduction

The controlled living polymerization of monomers with unprotected amine side groups is a challenge for polymer chemists. Depending on the monomer and choice of technique, various problems can be encountered. For instance, the polymerization of monomers functionalized with primary amines using RAFT will not proceed in a controlled fashion due to the reaction between the amine and the carbon-sulfur bond in the RAFT agent[1]. In the case of ROMP, the situation has been historically difficult for metal-carbene mediated polymerizations as the amine is believed to poison the catalyst[2]. As a result, amine functionality has traditionally been incorporated into polymers made by ROMP, by the use of amine protected monomers. Although, very little literature has been presented regarding this area, some publications describe the polymerizations of protected amines. Tew and coworkers polymerized a series of Boc protected norbornenes to obtain polymers with a wide range of MWs (1.6 – 137.5 kDa) and narrow PDIs (1.1-1.3). the antibacterial activity determined by growth inhibition assays and the hemolytic activity against human blood cells were measured and compared to determine the selectivity of the polymers for bacterial over mammalian cells[3]. Figure 3.1 shows the molecules synthesized by Tew.

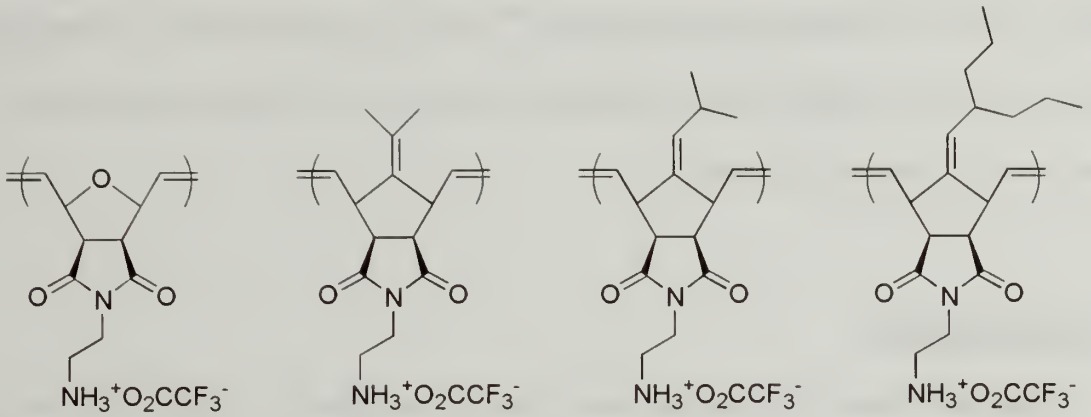


Figure 3.1 Polymers synthesized by Tew and coworkers.

Lowe and coworkers synthesized norbornenes quarternized with various alky halides[4]. Using Grubbs' 1st generation catalyst Lowe was able to produce polymers with MWs and PDIs between 7.7 and 25 kDa and 1.07-1.24. Figure 3.2 shows the monomers synthesized by Lowe and coworkers.

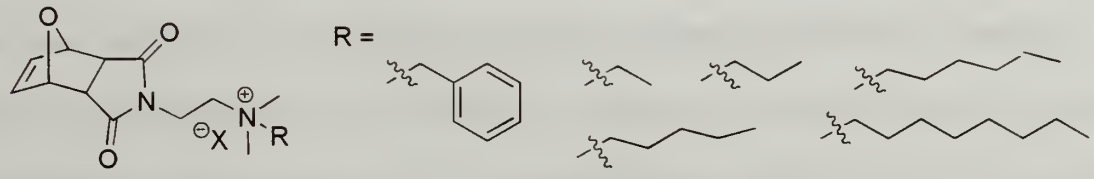


Figure 3.2 Monomers synthesized by Lowe and coworkers.

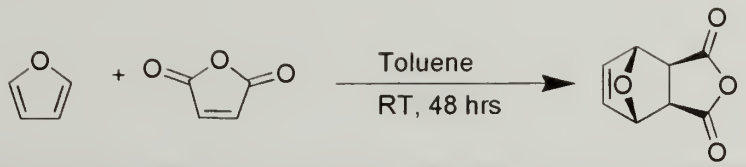
Setton and coworkers polymerized norbornenes that were functionalized with short peptide sequences[5]. These monomers are shown in scheme 1.3. The Boc group was used to protect the terminal amines in these peptides. The researchers referenced thus far have all used protecting groups to achieve controlled polymerizations using ROMP. With the exception of Lowe, who designed a polar solvent system to polymerize quarternized norbornenes. Although, in all cases polymers with good control over MW and PDI were obtained, protection-deprotection chemistry was still used. In this chapter, we present the synthesis of a bis amine functionalized norbornene

monomer. That was polymerized using Grubbs' 3rd generation catalyst in THF *without* protection chemistry or the use of highly polar or chlorinated solvents. The solution properties of this polymer will be presented in chapter 6.

Experimental Section

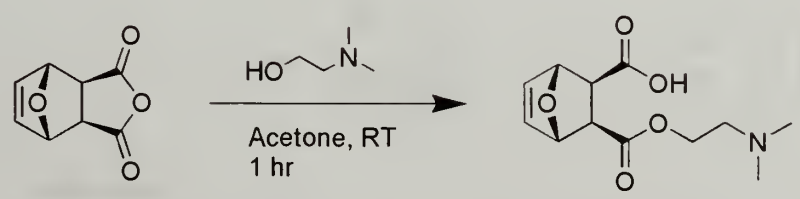
Materials. Furan (99%) was purchased from Sigma-Aldrich and used as received. Maleic anhydride (99%) was obtained from Fluka and used without further purification. N, N-Dimethylaminoethanol (98%) obtained from Sigma-Aldrich was used as is. Diisopropyl azodicarboxylate (DIAD) (95%) was purchased from Sigma-Aldrich. Triphenylphosphine (PPh_3) (95%) was obtained from Fluka. THF was distilled over sodium and benzophenone under nitrogen prior to use.

Synthesis of Oxo-Norb-Diamine. Synthesis of Oxo-Norbornene anhydride was done according to a modified procedure of Furdik [6]. A 250 mL beaker containing 200 mL of toluene was charged with 25 g (0.25 mol) of maleic anhydride. The mixture was stirred for 30 mins after which the undissolved residue was filtered. Furan, (22 mL, 0.30 mol) was then added to the saturated maleic anhydride solution and the reaction was stirred vigorously for 48 hrs at room temperature (Scheme 3.1).The precipitate was then filtered and washed several times with toluene and hexane and dried for 12 hrs in a vacuum oven to give 36g (yield = 88%) of a white solid. Mp 119°C, ^{1}H NMR (300 MHz, $DMSO_6$) δ 3.35 (s, 2H), 5.39 (s, 2H), 6.62 (s, 2H). ^{13}C NMR (75MHz, $DMSO_6$) δ 49.9, 83.1, 137.7, 171.9.



Scheme 3.1 Synthesis of *exo* 7-Oxabicyclo [2.2.1] hept-5-ene-2, 3-dicarboxylic anhydride.

A 200 mL beaker was charged with 150 mL of acetone and 20 g (0.12 mol) of *exo* 7-oxabicyclo [2.2.1] hept-5-ene-2, 3-dicarboxylic anhydride. To this solution 18 mL (0.18 mol) of N, N-dimethylaminoethanol was added at once and the reaction was left for 1 hr at room temperature (Scheme 3.2). The resulting precipitate was filtered and washed with cold acetone followed by hexane and then dried for 2 hours in a vacuum oven. The zwitterionic product (29g, yield = 95 %) obtained as a white solid was used without further purification. ^{1}H NMR (300 MHz, $DMSO_6$) δ 2.38 (s, 6H), 2.55 (q, J= 7.2Hz, 2H), 2.75 (t, J= 4.8, 2H), 4.13 (t, J= 6Hz, 2H), 4.99 (d, J= 6Hz, 2H), 6.35 (m, J= 17.1Hz).

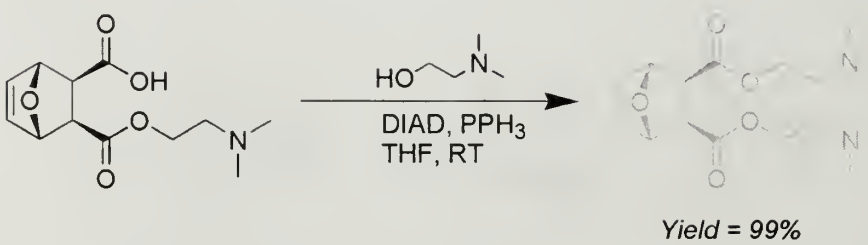


Scheme 3.2 Synthesis of *exo* Oxo-Norbornene Zwitterion.

A dry 250 mL round bottom flask was charged with 15g (0.058 mol) of oxo-norbornene zwitterion, 7.1 mL (0.07 mol) N, N-dimethylaminoethanol, 18.3g (0.07 mol) of PPh_3 and 200 mL of THF. The mixture was cooled to 0°C under nitrogen after which 14.1 mL of DIAD was added drop wise over 1 hr and the mixture left for 12 hrs (scheme 3.3).

The solvent was removed and the crude product dissolved in 100 mL of acidified water. This solution was then washed with 1 L ethyl acetate. The aqueous solution was made basic by the addition of potassium carbonate, and the diamine product was recovered by continuous extraction from diethyl ether: hexane (9:1) over 2 days. Oxo-Norb-Diamine was dried and obtained as an off-white solid (8g, recovered yield = 42.3%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 12H), 2.61 (t, J= 6Hz, 4H), 2.88 (s, 2H), 4.19 (m, 4H), 5.28 (s, 2H), 6.46 (s, 2H) (see figure 3.3) ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.57, 46.92, 57.57, 62.56, 80.66, 136.66, 171.58 IR cm^{-1} 1188 1739, 2973, 2945.FAB-MS m/z 327 (M^+). MP = 32°C.



Scheme 3.3 Synthesis of Oxo-Norb-Diamine.

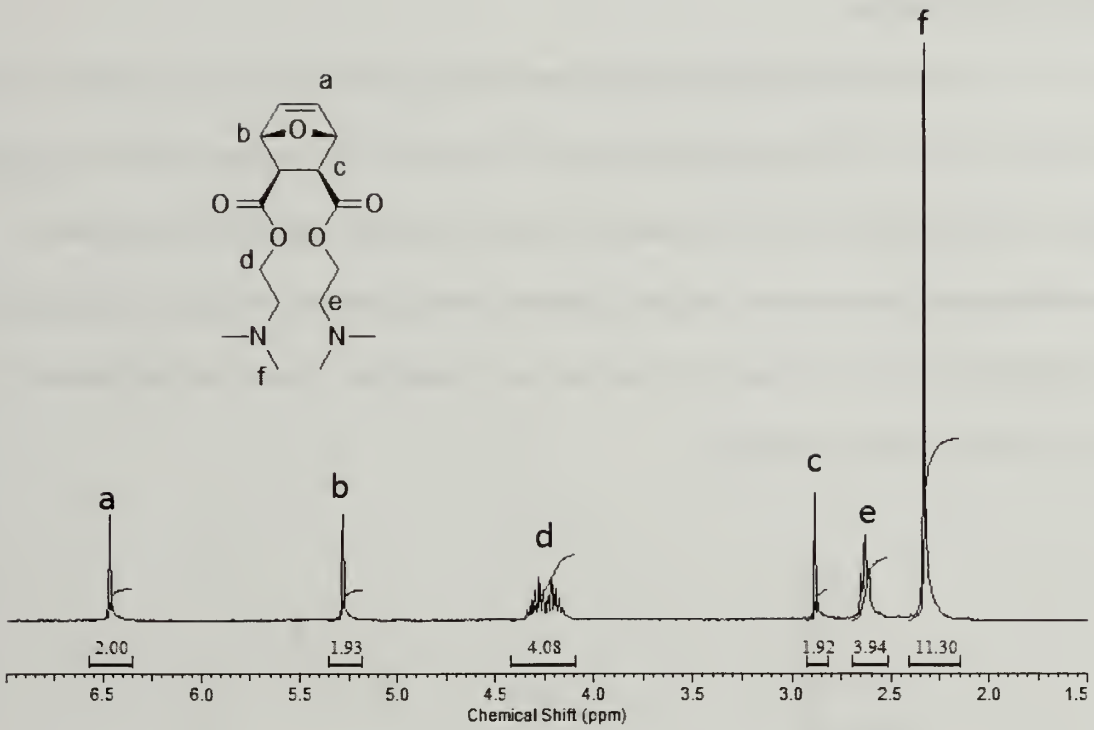


Figure 3.3 ^{1}H NMR spectrum of Oxo-Norb-Diamine in $CDCl_3$.

Polymerization of Oxo-Norb-Diamine. A Schlenk flask, charged with 0.1g (31 mmol) of oxo-norb-diamine, was placed under vacuum for 10 mins. Another Schlenk flask containing 3 mg (3.3 μmol) of G3 and a stir bar was evacuated for approximately 10 mins as well. Freshly distilled THF was degassed by 3 freeze-pump-thaw cycles, and 1 ml was then added to each flask. The monomer solution was then added to the catalyst solution and the reaction left for 7 mins. The reaction was terminated by the addition of 2 mL of ethyl vinyl ether. The polymer was then precipitated from cold hexane as a tacky dark green solid. Yield of polymer as determined by ^{1}H NMR and DMF GPC was 99%.

Results and Discussion

Table 3.1 shows polymerization data for oxo-norb-diamine. MWs obtained by DMF GPC are in very good agreement with predetermined MWs. The table also shows that we have excellent control over the polydispersity of the samples made. In addition, figure 3.5 shows that the polymerizations are mono modal. A plot of number average molecular weight versus degree of polymerization is shown in figure 3.4. This plot is a straight line which provides further evidence that these polymerizations are living.

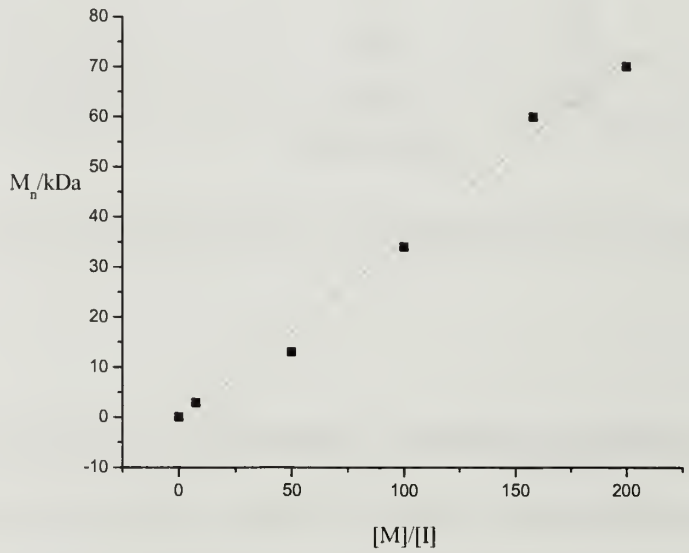


Figure 3.4 Plot of M_n vs. DP for PolyOxo-Norb-Diamine.

These results were very surprising and unexpected as amines are known to chelate to ruthenium based catalyst. In fact the synthesis of Grubbs' 3rd generation catalyst (scheme 2.3) involves the displacement of a phosphine ligand with a secondary amine. It has also been documented that amines are not compatible with ruthenium based ROMP catalyst; therefore, these observations seem to suggest something here is allowing polymerization. This suggests at least in this case the structure of the monomer strongly influences the polymerization. The secondary amines attached

to the norbornene could be somewhat less nucleophilic than their free counterparts. As a consequence, the rate of polymerization maybe much faster that the possible rate of nucleophilic addition between the secondary amines and the ruthenium center. This speculation is supported by the fact that N, N- dimethylaminoethanol added to a polymerization containing the diamine monomer does not yield high MW polymer. Further experiments are currently being performed to further clarify these findings.

Table 3.1. Polymerization data for Oxo-Norb-Diamine.

[M] /molL^{-1}	[I] molL^{-1}	Target M_n / kDa	[b]Obtained M_n / kDa	PDI	Yield /%
0.15	0.02	2	3	1.05	99
0.3	0.006	16	13	1.08	99
0.3	0.003	33	34	1.08	99
0.3	0.0019	51	60	1.08	99
0.3	0.0015	65	70	1.07	99

[a] *MWs obtained from GPC calibrated with linear polystyrene with DMF as eluent*

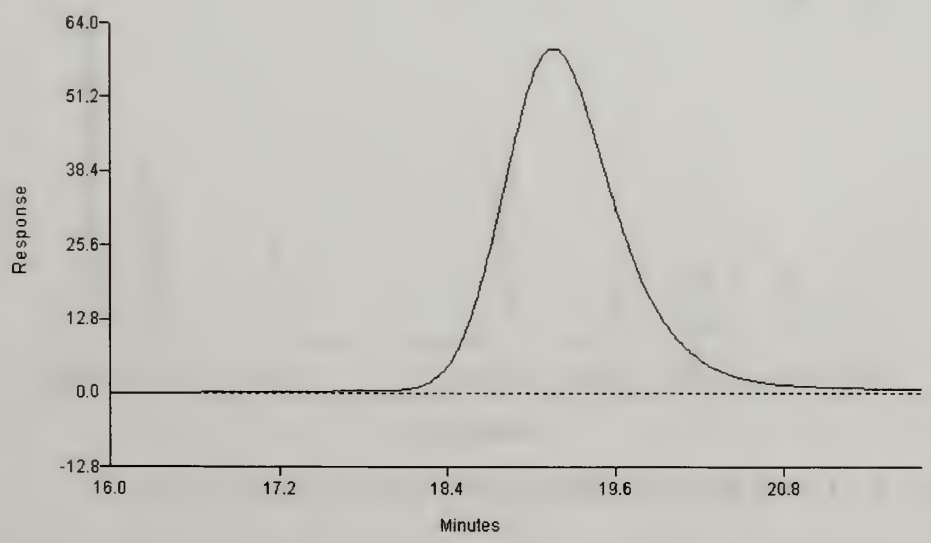


Figure 3.5 GPC trace for PolyOxo-Norb-Diamine with M_n = 34kDa, PDI = 1.08.

Figure 3.6 shows a typical ^{1}H spectrum for polymers obtained from oxo-norb-diamine. The polymerization dictates that there are vinyl groups along the backbone. The resulting vinyl protons can be either *cis* or *trans* (a, a') as seen from the signals between 4.5 -6.0 ppm. The protons adjacent to the oxygen bridge head are close enough to the vinyl protons to be split into two sets of protons (b, b'), those adjacent to the *cis* protons and those next to the *trans* protons. The protons (c) at 3.09 ppm are further away so that they are not strongly influenced by the vinyl protons, but they do show a slight double peak nonetheless, (see figure 3.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (br s, 12H), 2.53 (br s, 4H), 3.09 (br m, 2H), 4.15 (br s, 4H), 4.68 (br s, 1H), 5.06 (br s, 1H), 5.52 (br s, 1H), 5.85 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.58, 52.31, 53.07, 57.29, 62.85, 80.43, 130.66.

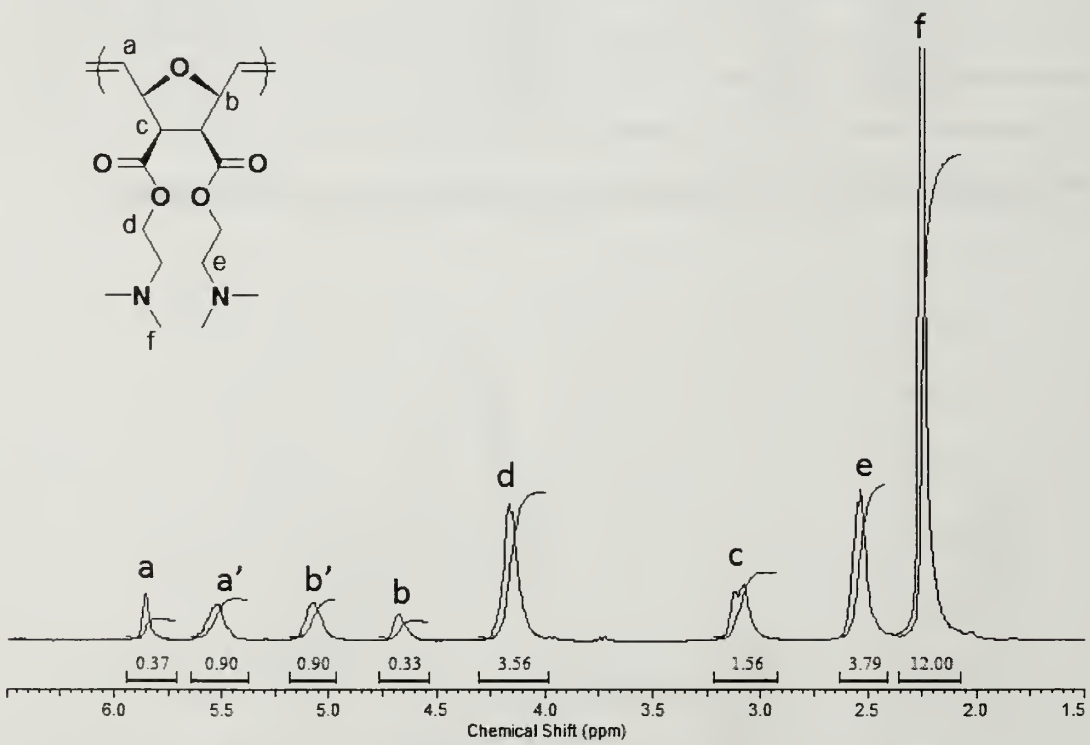


Figure 3.6 ^{1}H NMR spectrum of PolyOxo-Norb-Diamine in $CDCl_3$.

Amine functionalized polymers find various uses in industry. These include flocculating agents for the purification of water supplies, thickeners in the food industry, and antimicrobials in medicine and biomaterials[7-11]. Most of these applications rely on free radical chemistry to obtain high MW polymer, the use of ROMP on an industrial scale is not very feasible at the moment although it is steadily gaining momentum. This is due in part to the cost of the catalyst employed and low moisture and oxygen tolerance. Also high reactivity is needed to produce material in a timely manner. Although, Shcrock's catalysts[12, 13] are sufficiently reactive they are expensive and they still suffer from functional group intolerance and air sensitivity. Grubbs' 3rd generation catalyst used in this work has sufficient reactivity and can be used with many functional groups. This work demonstrates that we can indeed generate well defined amine containing polymers using ROMP.

One of the barriers to industrial use would be the cost of the catalyst, but this can be circumvented by utilizing Grubbs' 2nd generation catalyst. In this chapter we showed that we can functionalize norbornene anhydride monomer with one or two tertiary amine side groups in good yield and high purity. These bis functional monomers were easily polymerized and we were able to control the MW and the PDI of the resulting polymers. These polymers dissolved in water to give clear solutions. As mentioned earlier there are very few examples of the direct ROMP of amine functionalized norbornenes. Our success here provides a blue print for polymer chemist with an interest in norbornenes with amine side groups. The polymerization of this monomer represents to the best of our knowledge the first example of the direct polymerization and a norbornene monomer containing an unprotected amine. The monomers polymerized by Lowe and coworkers are similar however, quarternization of his amine groups could be considered a form of protection. This synthesis circumvents the need for protection-deprotection chemistry

thereby saving both time and resources. Also, the amine functionality is certainly present on every repeat unit. Additionally, two amine groups per repeat unit provide high functional group density which can be beneficial in certain applications such as antimicrobial surfaces and additives, and drug delivery. So far, chapters two and three detail the use of carboxylic acid and amine functionality to impart water solubility to norbornene polymers. The following chapter describes the use of PEO as another moiety to achieve water solubility.

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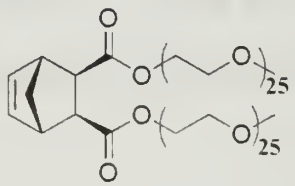
CHAPTER 4

A NON-IONIC WATER SOLUBLE POLYMER



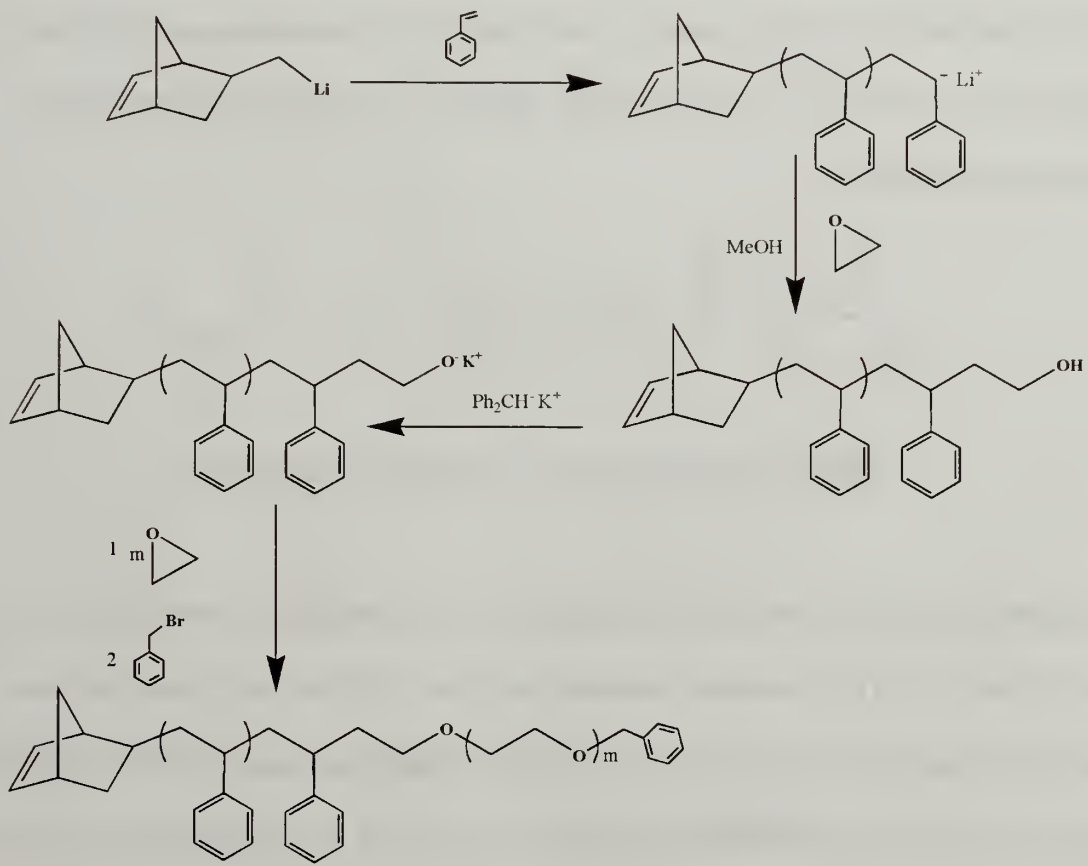
Introduction

Water-soluble polymers usually contain functionalized side groups that provide overall negative free energy interactions between the polymer chains and water molecules. These associations may be hydrogen bonding, dipole-dipole interactions, or ionic interactions. In the previous two chapters, the synthesis of water-soluble polymers that contained carboxylic acid and amine was presented. In these two cases, the (ionic) functionality provided water solubility. In this chapter, the synthesis and polymerization of a monomer that contains non-ionic side groups that impart water solubility will be shown. Water-soluble polymers are of great interest in drug delivery[1], biomaterials[2], dispersants[3], flocculants[4], and other soft material applications[5]. Poly(ethylene oxide) (PEO), a water soluble polymer, has attracted considerable attention and PEO functionalized polymers are wide spread in the literature[6-8].

With increasing interest in polymers for biomedical applications,[9-12] the use of poly(ethylene oxide) containing monomers continues to greatly expand[13]. *Densely grafted* water soluble polymers are particularly useful as they accomodate a large number of functional groups on much less volume than linear polymers of the same molecular weight. As has been extensively reviewed, they can be obtained by strategies such as 'grafting onto',

'grafting from', and via macromonomers[14]. The macromonomer approach, which is followed in this work, involves the synthesis of a monomer that carries a polymer side chain but still undergoes polymerization.

Compared to the bulk of PEO literature, very little work has been reported on PEO functionalized macromonomers which undergo ROMP). Gnanou and coworkers pioneered the synthesis of poly(ethylenoxide) macromonomers for ROMP: ethylene oxide was polymerized anionically from a norbornene functionalized initiator[15]. Their synthetic approach is shown in scheme 4.1.



Scheme 4.1 Macromonomers synthesized by Gnanou and coworkers.

Two polymer samples were made from these macromonomers each having MWs of 52 and 91.7 kDa, and PDIs of 1.15 and 1.10 respectively. Both monomers were reported to polymerize to complete conversion. They also investigated the use of PEO macromonomers as stabilizers in the synthesis of latex particles via ROMP[16, 17]. The same group used PEO macromonomers with long side chains (n=122) to stabilize norbornene-methyl methacrylate latex particles in aqueous emulsion[18]. While the original paper on the PEO macromonomer[19] only characterizes the macromonomer and the resulting polymers in organic solution, none of the following works demonstrate full water solubility of this polymer, although its usefullness as a surfactant and comonomer in emulsion and dispersion polymerization was beautifully demonstrated. More recently, short chain PEO macromonomers (n=4) were used by Runge and coworkers[20] as a monomer (see figure 4.1) in complicated comb block copolymer architectures.

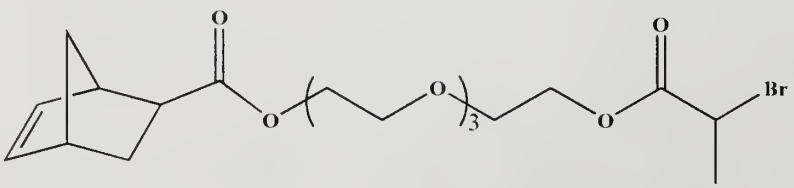


Figure 4.1 Macromonomer synthesized by Runge et al.

Breitenkamp and Emrick[21] reported the synthesis of a macromonomer whose structure is shown in figure 4.2. This monomer contained only three ethylene oxide units and was polymerized in acidified water using a water soluble ruthenium catalyst. MWs between 67-137 kDa were reported with PDIs ranging from 1.35 to 2.37. Average yields were noted to be 80%.

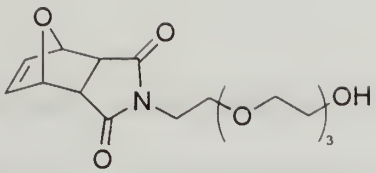


Figure 4.2 Macromonomer synthesized by Emrick and coworkers.

While Biagini et al. described the synthesis of a very similar monomer containing five EO repeat units[22]. These authors showed that copolymers and block copolymers containing this repeat unit are not fully water-soluble. This is most likely due to the short side chain length of these repeat units which fail to compensate for the hydrophobicity of the backbone and the other comonomers.

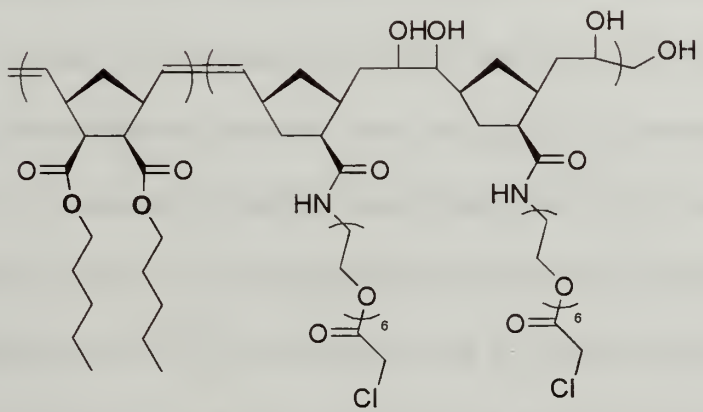


Figure 4.3 Block copolymer synthesized by Kane et al.

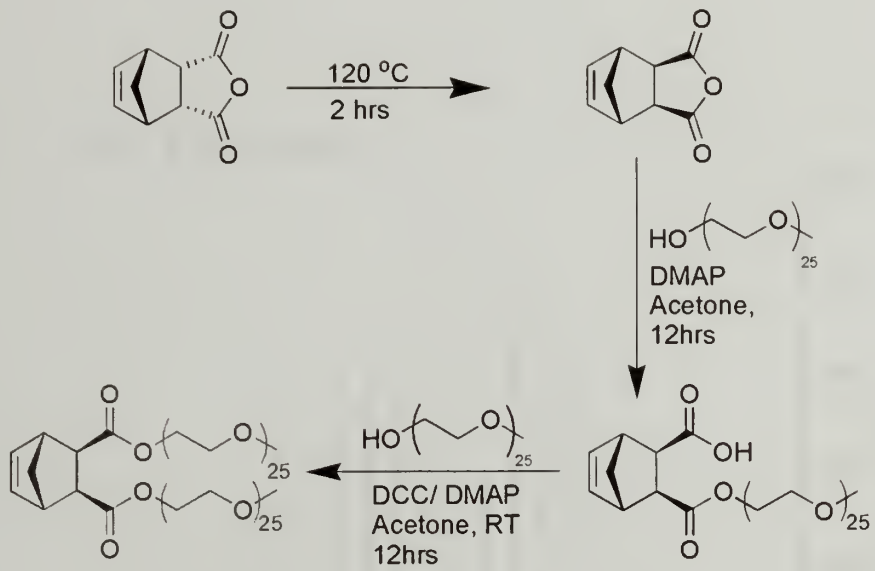
Kane et al. describe block-copoylmers with poly(ethylene oxide) side chains obtained by post polymerization functionalization, however these polymers were designed to form micelles rather than to be molecularly soluble in water[23](see figure 4.3).

In summary, the water solubility (meaning single chains, not aggregates or colloidally soluble species) of this commonly used macromonomer and its homopolymer has not been demonstrated despite the fundamental importance of this property for many applications.

Experimental Section

Materials. 5-norbornene-2, 3-dicarboxylic anhydride (*endo*) (99%) was obtained from TCI. Polyethylene oxide monomethylether (PEG M_n = 1.1 kDa) was purchased from Fluka and heated at 120°C under nitrogen for 2 hours prior to use. *N*, *N*-Dicyclohexylcarbodiimide (DCC) (99%) was purchased from Fluka and used as received. 4-(Dimethylamino) pyridine (DMAP) (99%) was purchased from Sigma-Aldrich. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under nitrogen prior to use.

Synthesis of Norb-DiPEG. The synthesis of the precursor anhydride, *exo*-5-norbornene-2, 3-dicarboxylic anhydride, was outlined in chapter 2. A 100 mL round bottom flask was charged with 0.5g (0.003 mol) of *exo* anhydride precursor, 6.7g (0.006 mol) of PEG 1100, 3.6mg (30μmol) of DMAP, 1g (0.0048 mol) of DCC and 25 mL of acetone. This mixture was stirred at room temperature for 2 day, after which the white precipitate was filtered. The filtrate was concentrated under vacuum and the product purified by dissolution in dichloromethane followed by precipitation from diethyl ether. This process was repeated 3 times to yield a white solid which was dried and weighed to give 4.6g (yield = 65%) of Norb-DiPEG (scheme 4.2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (d, J= 1.2Hz, 1H), 1.66 (d, J= 1.2 Hz, 1Hz), 2.65 (s, 2H), 3.10 (s, 2H), 3.38 (s, 3H), 3.65 (s, 4H), 3.88 (m, 2H), 4.11 (m, 2H), 4.27 (m, 2H), 6.21 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 70.58. IR cm^{-1} 958, 1101, 1741, 2884.



Scheme 4.2 Synthesis of Norb-DiPEG.

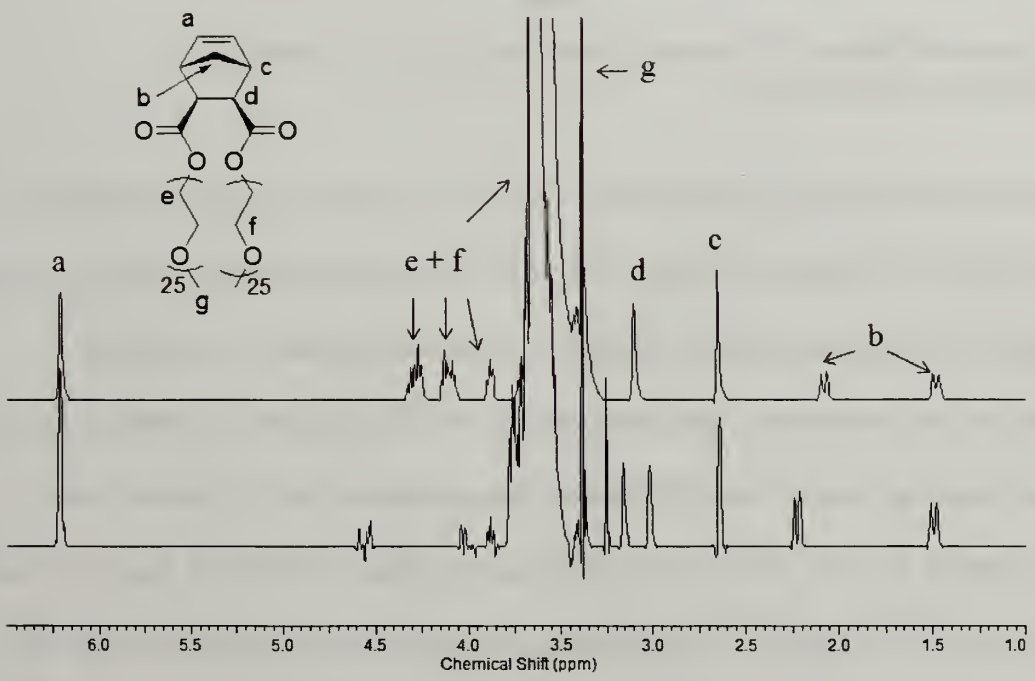


Figure 4.4 ^{1}H NMR spectrum of Norb-DiPEG (top) and intermediate in $CDCl_3$.

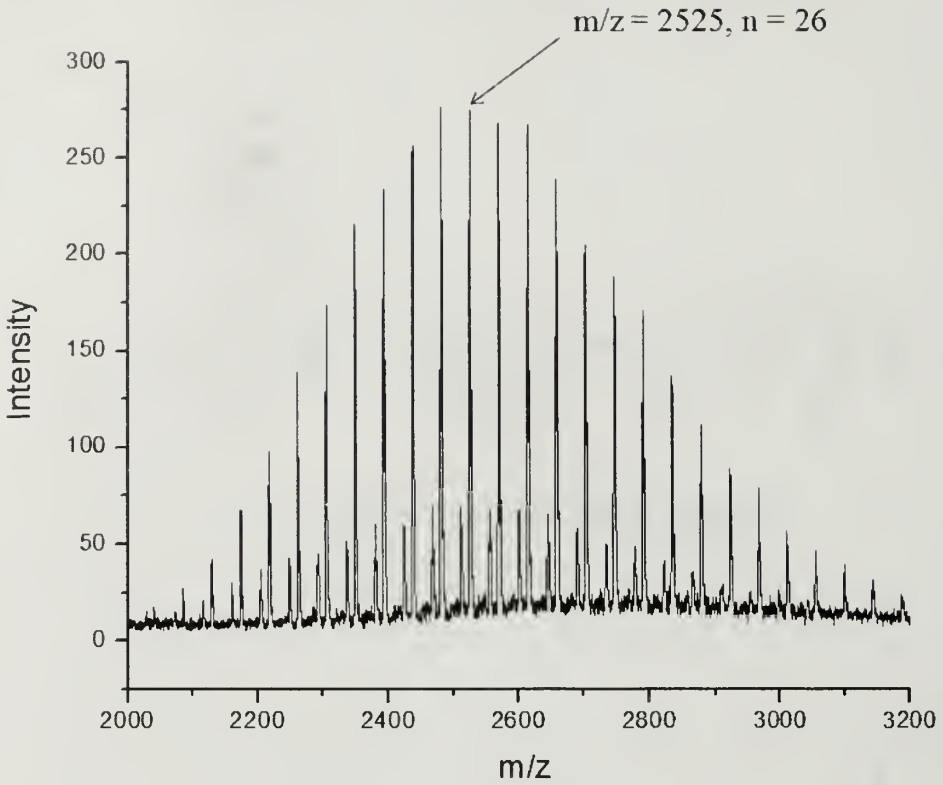


Figure 4.5 Maldi-TOF spectra of Norb-DiPEG in THF. Matrix = 2, 4-dihydroxybenzoic acid.

Figure 4.4 shows the ^{1}H NMR spectrum of Norb-DiPEG (top spectrum) and intermediate (see scheme 4.2) in $CDCl_3$. The peaks at 3.0 and 3.2 ppm in the in the intermediate coalesce into one peak at 3.1 ppm for the macromonomer as a result of increased symmetry. This is good indication that the macromonomer is functionalized with two PEG chains. To further confirm the structure of the macromonomer, Norb-DiPEG was characterized by Matrix Assisted Laser Desorption Ionization Time-of- Flight mass spectroscopy (MALDI –TOF MS). Figure 4.5 shows the spectrum obtained. MALDI-TOF is particularly good at determining end-groups provided that the molecule in question ionizes fairly well. From the spectrum we observe two distributions which can be readily accounted for. The major distribution is our target molecule which is

confirmed by analysis of the individual peaks. Our macromonomer can be envisioned as PEG that is end functionalized. Thus the end groups here would be the norbornene anhydride moiety and the methyl groups. The counter ion used in this experiment was sodium so that all m/z values have an additional value of 23. For illustration, the peak labeled 2525 Da was chosen. This value corresponds to two PEG chains with a repeat unit of 26 (n) for each chain, the end group molecular weights are 212 (one norbornene anhydride and two methyl fragments), and one sodium counter ion. If we sum these values, $(44 \cdot 26) \cdot 2 + 212 + 23$, we obtain a m/z of 2523 Da. For the minor distribution a similar analysis indicates that the methyl groups are substituted by hydroxyl groups.

Polymerization of Norb-DiPEG. In a typical experiment, 5 mL of THF was degassed by three freeze-pump-thaw cycles. 0.20 g (55 μmol) of monomer and 2 mg (2.2 μmol) G3 were then placed in two reaction vessels and evacuated for five minutes. A Hamilton syringe was then used to introduce 1 mL of THF to the monomer flask and 0.5 mL of THF to the catalyst. The solutions were further degassed by an additional freeze-pump-thaw cycle. After reaching room temperature, the monomer solution was added to the G3 solution and the reaction was stirred vigorously for 20 minutes. The polymerization was terminated by the addition of 2 mL of ethyl vinyl ether. The polymer was then precipitated from diethyl ether to yield an off-white powder. (Yield = 85 %) ^{1}H NMR: (300 MHz, $CDCl_3$): δ 1.21 (bs, 1H), 1.73 (bs, 1H), 2.06 (bs, 2H), 2.84 (bs, 2H), 3.39 (s, 3H), 3.65 (bs, 4H), 3.89 (m, 1H), 4.14 (bs, 4H), 5.20 (bs, 1H), 5.41 (bs, 1H).

Results and Discussion

The synthesis of Norb-DiPEG is shown in Scheme 4.2. Attachment of PEG followed a two step process as shown in scheme 4.2. First, the anhydride was ring opened by PEG with (DMAP) as catalyst. Then, ester coupling conditions were used to attach the second arm of PEG to the remaining free carboxylic acid in 65 % yield. This design allows easy attachment of various PEG chain lengths, or other functionalities. Also, asymmetrical monomers with different functional groups can be synthesized as shown by the intermediate in Scheme 4.2 (the mono PEG, mono acid monomer).

Figure 4.4 shows the proton NMR for Norb-DiPEG (top spectrum) in $CDCl_3$ with the characteristic olefin, bridge-head, and PEG peaks which confirm the structure. This monomer was easily polymerized, at concentrations above 0.037 mol/L, to 90 % yield in 7-40 minutes depending on the desired molecular weight. Typically, the degassed monomer solution was added to a solution of the Grubbs' Catalyst. The reverse addition was also performed with no adverse affects on the polymerization. The analytical data for these polymerizations are summarized in Table 4.1, which shows that we have very good control over the polymerization of this monomer with molecular weights ranging from 35-99 kDa. The number average molecular weights obtained from gel permeation chromatography (GPC) in THF (calibrated with polystyrene) were all approximately half the targeted ones. This disparity can be attributed to different hydrodynamic volumes of these polymers compared to the calibration standard. Additionally, polymers from Norb-DiPEG are all comb-like in architecture. It has been shown that comb-like polymers display molecular weight values that are much less than expected based on GPC [24, 25].

Figure 4.6 shows a typical GPC curve for polymers generated from Norb-DiPEG. As can be seen, the line profile is perfectly symmetrical with no observable high or low molecular weight shoulders, which can occur when macromonomers are polymerized.

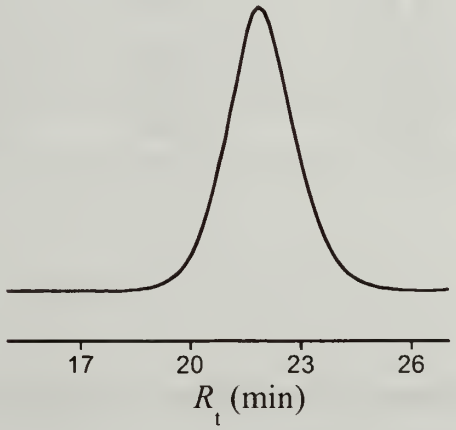


Figure 4.6 GPC trace for PolyNorb-DiPEG with M_n = 20kDa, PDI = 1.14.

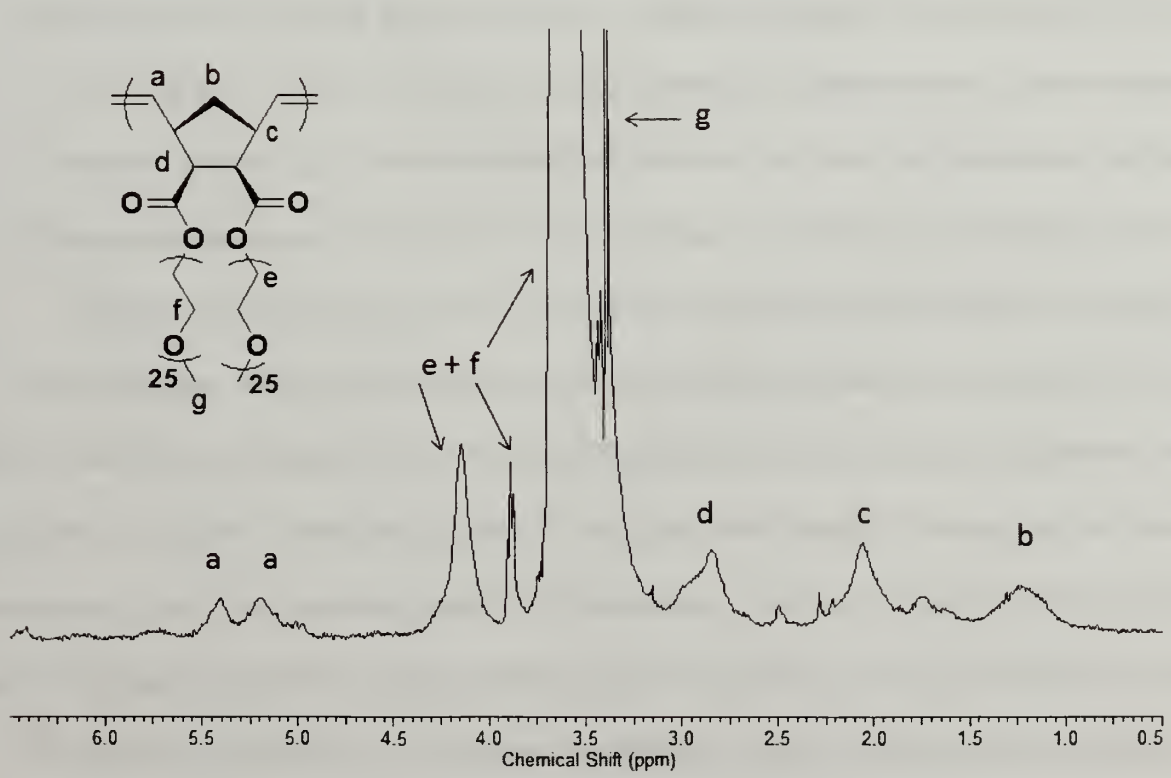


Figure 4.7 ^{1}H NMR spectrum of PolyNorb-DiPEG in $CDCl_3$.

Table 4.1. Polymerization data for Norb-DiPEG.

[M] x 10^{-2} /molL^{-1}	[I] x 10^{-3} /molL^{-1}	DP	$M_{n,\ calculated}$ /kDa	$M_{n,\ GPC}$ /kDa	PDI	Conversion /%
2.7	2.8	10	35	14	1.15	90
5.5	4.2	13	42	20	1.14	90
7.3	2.2	16	51	23	1.10	90
9.7	3.5	27	99	50	1.04	90

Conclusions

In this chapter we have demonstrated a facile synthesis to attach PEO chains to a norbornene monomer. These monomers were well characterized and shown to readily undergo ROMP using Grubbs' 3rd generation catalyst. Previous research groups have accomplished similar success, but this method is advantageous for a number of reasons. First fairly easy synthetic methodologies were used to obtain the macromonomers; ring opening reactions at ambient temperature and mild ester coupling. This is in contrast to the monomers prepared by Gnanou who attached PEO by anionic polymerization from a functionalized norbornene precursor. Second, our process is amendable to the synthesis of asymmetric macromonomers. The carboxylic acid group on the intermediate in scheme 4.2 can be readily reacted with a wide variety of groups to add different functionality to the resulting polymers. Third, our polymers are densely grafted polymers since they contain two PEO chains per repeat unit. Finally, polymers from Norb-DiPEG are visibly soluble in water, polymers made by Gnanou and Emrick were not reported to be water soluble. Dynamic Light Scattering data will be presented in chapter 6 to prove the molecular dissolution of these polymers. Our synthetic approach allows us to produce

polymers with good control over MW and PDI and this facilitates block copolymer synthesis which will be reported in chapter 6.

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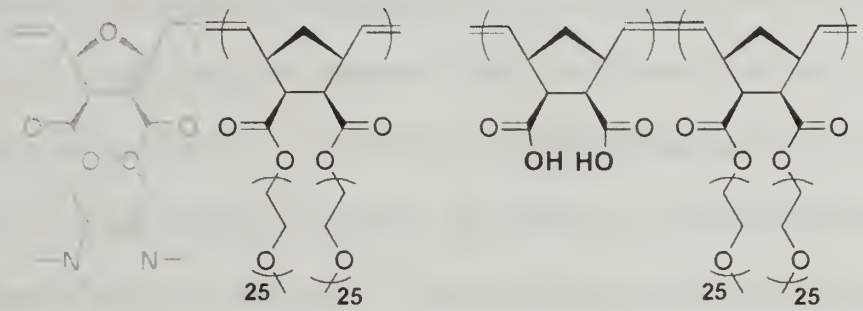
CHAPTER 5

DOUBLE HYDROPHILIC BLOCK COPOLYMERS



Introduction

One of the goals of polymer chemist is to achieve precise control over the architecture and accompanying properties of synthetic macromolecules. There are numerous synthetic routes to prepare copolymers with defined composition and topology. By adjusting monomer ratio and side groups, the physical, mechanical and electronic properties of a material can be systematically tuned. Efforts towards this end have resulted in new, well defined initiator systems for ring opening metathesis polymerization of functionalized norbornene monomers that enable synthesis of well defined block copolymers [1-12] .

Of particular interest are two water-soluble block copolymer motifs typically distinguished as amphiphilic block copolymers and double-hydrophilic block copolymers (DHBCs). Amphiphilic block copolymers are composed of a hydrophobic water insoluble block that associates in water and a hydrophilic block that prevents aggregates from precipitating[13-15]. DHBCs exhibit "schizophrenic" micellization behavior due to the water solubility of one or both blocks. They can self-assemble and form micellar or "reverse" micellar structures in water if external conditions such as temperature, pH, and ionic strengths are properly tuned[16-25]. Most DHBCs contain N-isopropylacrylamide (NIPAM), diallyldimethylammonium chloride

(DADAC), acrylic acid (AA), and PEO functionalized monomers[26-36]. The particular structure of DHBCs, facilitates physical or chemical transformations of one of the blocks in aqueous solution to render this block insoluble, the copolymer itself remaining dispersed by virtue of the hydrophilicity of the other block. Many DHBC monomers are readily polymerized by controlled polymerizations techniques such as RAFT or ATRP[16, 21, 25, 37, 38]. PEO can be polymerized by anionic ring-opening polymerization. Although, advances have been made in the synthesis of amphiphilic block copolymers made from ROMP[39-41], this technique has only been applied to the synthesis of one DHBCs[42]. Figure 5.1 shows this block copolymer, made by Lowe and coworkers.

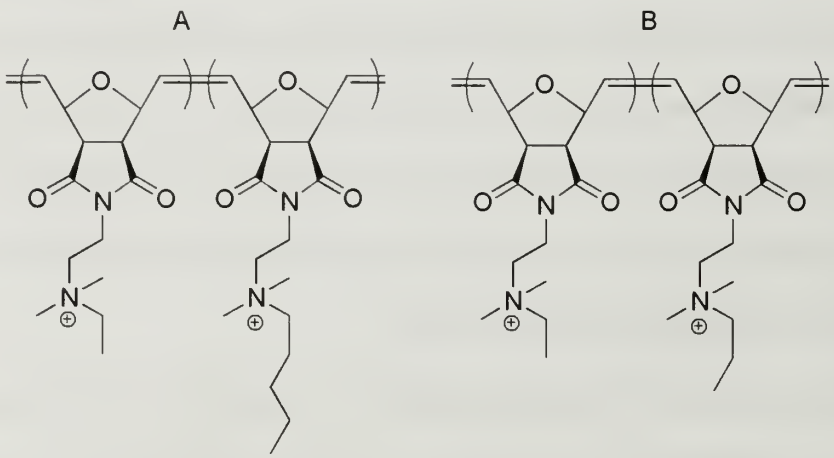


Figure 5.1 Double Hydrophilic block copolymers made by Lowe and coworkers.

These block copolymers were synthesized using Grubbs' 1st generation catalyst with 2, 2, 2-trifluoroethanol/methylene chloride mixture as the reaction medium. Sample A was reported to have a MW of 18.9 kDa and a PDI of 1.07. Sample B was also well controlled, with MW and PDI listed as 21.5 kDa and 1.12 respectively. Previous chapters demonstrated that we can control the homopolymerization of ionic and non-ionic functionalized monomers, a prerequisite for

block copolymer synthesis. In this chapter we explore the possibilities of synthesizing DHBCs from functionalized norbornene monomers.

Experimental Section

The synthesis of monomers used in this research was described in chapters 2-4. Polymerization to generate diblock copolymers was achieved as follows: a predetermined amount of G3 and ~2mol% (to monomer) BHT, Oxo-Norb-Diamine or Norb-Diacid, and Norb-DiPEG were placed in three separate Schlenk flasks and evacuated. Freshly distilled THF was degassed by three freeze-pump-thaw cycles and then added at a ratio of 1mL per 0.1 g of monomer to each flask (1mL was added to G3). A Hamilton syringe was then used to introduce the first monomer, Norb-Diacid, to the catalyst solution followed by the second monomer after a certain amount of time. After consumption of the second monomer the reaction was terminated with ethyl vinyl ether. The polymer was then recovered by precipitation from diethyl ether and dried under vacuum overnight.

Results and Discussion

Table 5.1. Polymerization data for Poly (Norb-Diacid-*b*-Norb-DiPEG).

Block Ratio	[M1] /molL^{-1}	[M2] /molL^{-1}	[G3] /molL^{-1}	DP1	DP2	$M_{n,\ calculated}$ kDa	$M_{n,\ GPC}$ kDa	PDI
1:5	0.018	0.09	0.0037	5	25	80	30	1.05
5:1	0.1	0.02	0.0017	60	12	49	27	1.05
1:1	0.018	0.018	0.0014	13	13	44	28	1.06

MWs obtained from GPC calibrated with linear polystyrene with THF as eluent. Polymer samples were methylated prior to injection to prevent irreversible absorption to the columns.

Table 5.1 shows polymerization data for diblock copolymers formed from Norb-Diacid and Norb-DiPEG. [M1] and [M2] represent the acid and PEG-functionalized monomers concentrations and DP1 and DP2 are the targeted degrees of polymerization for each block respectively. Three different block ratios were synthesized with targeted and obtained MWs shown. The MWs were determined by GPC in N, N-dimethylformamide calibrated with poly (styrene). As was the case for polyNorb-DiPEG, the MWs obtained were all approximately half of the targeted values. In each case however, the PDIs were all very small in the range 1.05-1.06. Furthermore, figure 5.2 shows a typical GPC trace for these polymers that is symmetrical, indicating fast initiation and no chain transfer reactions. Yields between 90-95 % were obtained as determined by gravimetry.

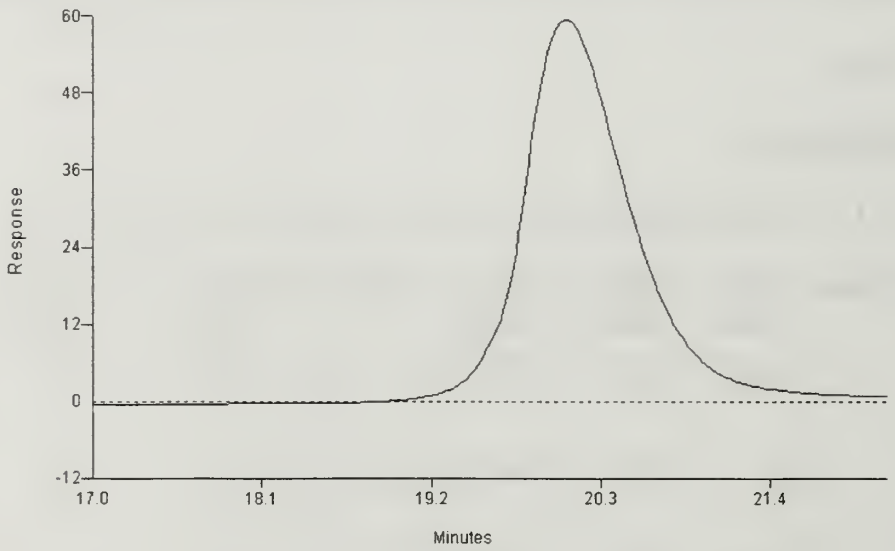


Figure 5.2 GPC trace for Poly (Norb-Diacid-*b*-Norb-DiPEG) with M_n = 30kDa, PDI = 1.05 block ratio = 1:5.

Table 5.2. Polymerization data for Poly (Oxo-Norb-Diamine-*b*-Norb-DiPEG).

Block Ratio	[M1] /molL^{-1}	[M2] /molL^{-1}	[G3] /molL^{-1}	DP1	DP2	$M_{n,\ calculated}$ kDa	$M_{n,\ GPC}$ kDa	PDI
1:5	0.005	0.025	0.0011	5	25	82	88	1.08
5:1	0.05	0.01	0.0013	38	8	38	49	1.07
1:1	0.025	0.025	0.0016	16	16	56	58	1.06

MWs obtained from GPC calibrated with linear polystyrene with DMF as eluent.

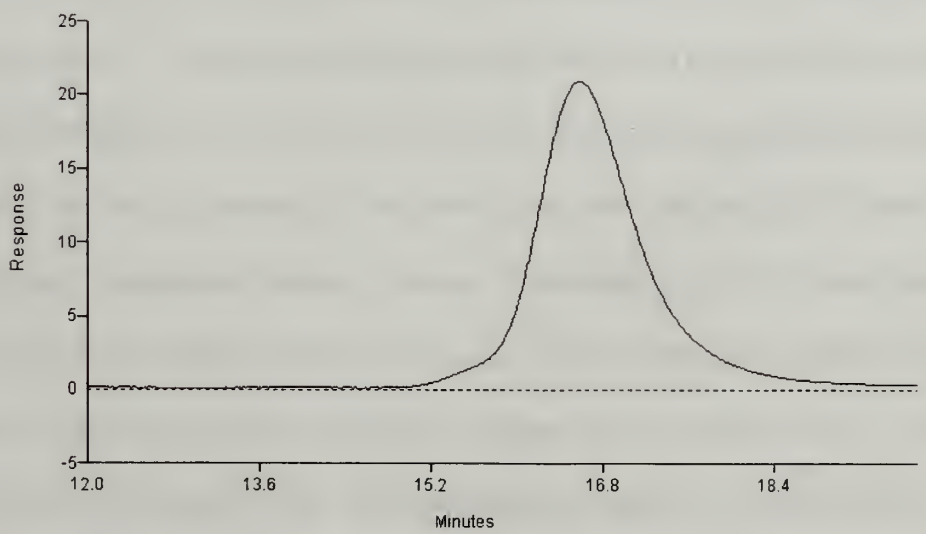


Figure 5.3 GPC trace for Poly (Oxo-Norb-Diamine-*b*-Norb-DiPEG) with M_n = 88kDa, PDI = 1.08. block ratio = 1:5.

Table 5.2 list polymerization data for three diblock copolymers made from Oxo-Norb-Diamine and Norb-DiPEG. This table shows that we have good control over the MW and PDIs of the resulting polymers. Figure 5.3 shows a typical GPC chromatogram for the block copolymers. They are generally symmetric with a slight hump observable on the high molecular weight side. This feature negligibly affects the polydispersity, determined by integration from roughly 14 to 19 minutes on the chromatogram (figure 5.3). All MWs determined by GPC are in close agreement to the theoretical values. This result is not expected, as all previous MWs obtained for Norb-DiPEG samples are lower than the targeted values. For comb-like polymers, like polyNorb-DiPEG, the length of the side chain influences the stiffness of the backbone which affects the hydrodynamic volume of the polymer in solution. Longer side chains increase the stiffness more than shorter chains, and as a result polymers, with longer side chains generally have a larger hydrodynamic volume and elute faster on the GPC column. This is not the only factor affecting elution time, as polymers from Norb-DiPEG (table 4.1) and other comb-like polymers have been shown to have MW that are lower than expected[43, 44]. This argument can also be applied to block copolymers formed from Norb-Diacid and Norb-DiPEG. It should be noted here that all diacid samples were methylated prior to injection on the GPC columns, so that any interaction between acidic groups and the packing material was minimal. For poly (norb-diacid-*b*-norb-DiPEG), the influence of the diacid block does not seem to influence the hydrodynamic volume significantly as compared to polynorb-DiPEG, and hence the MW trend obtained for these diblocks is similar to polynorb-DiPEG. (MW obtained is lower than targeted MW). For the diamine copolymers the influence of the comb-like DiPEG block is minimized and a MW closer to the expected value is obtained. A possible explanation is that DMF is a very

good solvent for both blocks of the diamine copolymers, whereas THF is a good solvent for polynorb-DiPEG but a poor solvent for the diacid block.

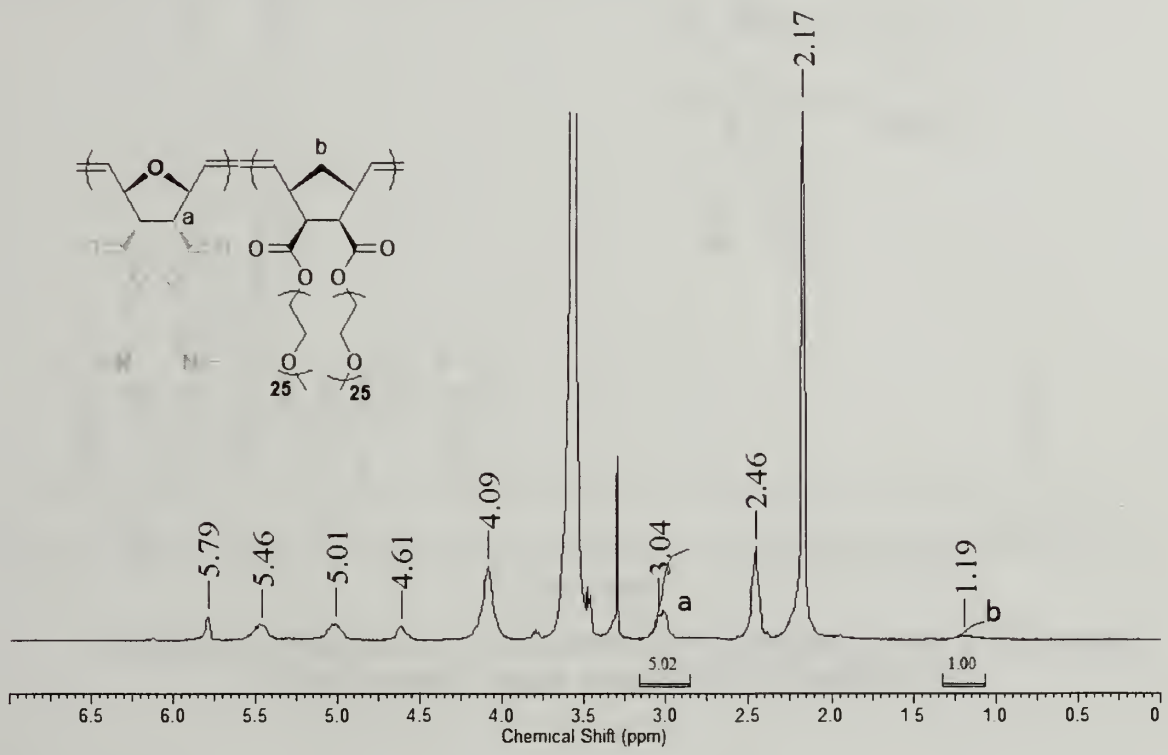


Figure 5.4 ^{1}H NMR spectrum of Poly (Oxo-Norb-Diamine-*b*-Norb-DiPEG) in $CDCl_3$.M_n = 88kDa, PDI = 1.08 block ratio 5:1 (amine: PEG).

Figure 5.4 shows a typical ^{1}H NMR spectrum of Poly (Oxo-Norb-Diamine-*b*-Norb-DiPEG). For this sample, a block ratio of 5:1 (amine: PEG) was targeted. From the spectrum we can compare the signal at 3.04ppm, which is characteristic of the proton alpha to the carbonyl group in the amine, and the signal originating from the PEG block at 1.19ppm. The spectrum shows that we have very good experimental and theoretical agreement for the block ratios. This adds additional support for our ability to synthesize diblock copolymers with good control over MW and polydispersity.

Figure 5.5 ^{1}H NMR spectrum of Poly (Norb-Diacid-*b*-Norb-DiPEG) in $DMSO_6$. M_n = 27kDa, PDI = 1.05 block ratio 5:1 (diacid: PEG).

Figure 5.5 shows ^{1}H NMR spectrum of Poly (Norb-Diacid-*b*-Norb-DiPEG) in $DMSO_6$ which is typical for all diacid-diPEG block copolymers synthesized. For these polymers block ratio determination was approximated by comparing the signal at 1.70ppm and the acidic protons at 12.51ppm. A value of ~ 4:1 diacid to diPEG was obtained which is close to the targeted block ratio.

Both sets of diblock copolymers dissolve in water to give visibly clear solutions at all pH values. However, this does not indicate strict water solubility, i.e., existence in aqueous solution as single chains, as it is possible to form aggregates between 20-60nm that are invisible to the eye. A closer look at the solution properties of these diblocks will be presented in following chapter. Although these diblocks can be considered DHBCs, they show a distinction from traditional DHBCs in that they may not form micelles or reverse micelles in

water. One possible method that can be used to achieve micellization is to quarternize the amine groups in Poly (Oxo-Norb-Diamine-*b*-Norb-DiPEG) with a highly hydrophobic alkyl halide. This increases the hydrophobicity of the amine containing block which should then form the core of aggregated structures.

In this chapter we demonstrated that we can synthesize diblock copolymers from functionalized ionic and non-ionic monomers. GPC results show that we have excellent control over the MW and PDI, and all copolymers dissolve in water to give clear solutions. This is a very interesting synthesis as it provides one of the first examples of the use of ROMP to generate block copolymers with acidic and basic side groups without the use of protection-deprotection chemistry. These polymers also add to the very small library of DHBCs made from ROMP. The ease of monomer synthesis and facile polymerization makes studying structure-property relations easy, as many samples can be generated relatively quickly

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CHAPTER 6

LIGHT SCATTERING STUDIES

Introduction

The main goal of this thesis was to synthesize water-soluble polymers from norbornene anhydride monomers, an endeavor presented in previous chapters. Although there are no strict definitions of water solubility, our criterium will be of polymer as a single solvated chain in aqueous solutions. All these polymers dispersed in water to give visibly clear solutions, but this fact alone does not meet our afore mentioned criteria for water solubility as polymers can dissolve to form aggregated structures (micelles, micellar clusters) that are 20 – 60 nm in size, too small to be evident to the naked eye. Thus, to determine water solubility, light scattering methods were used. Static light scattering (SLS) is commonly used to determine the weight average molecular mass of polymers as well as their virial coefficient and size in solution. Furthermore, this method is absolute, so no calibration is required. Figure 6.1 shows the specific ALV instrument used for our light scattering experiments. A laser beam is focused onto the sample by an optical lens. The small scattered fraction of light is measured at a variable range of angles by a photomultiplier. The range of angles is 25° to 150°. When an electromagnetic wave impinges on a polymer/particle, the wave induces a dipole that oscillates and emits electromagnetic waves. The magnitude of the induced dipole moment is proportional to the polarizability of the polymer/particle and the oscillating electric field strength of the incoming beam. For polymer solutions, solution density and local polymer concentration fluctuations occur, and scattering is due to corresponding local fluctuations of the polarizability [2].

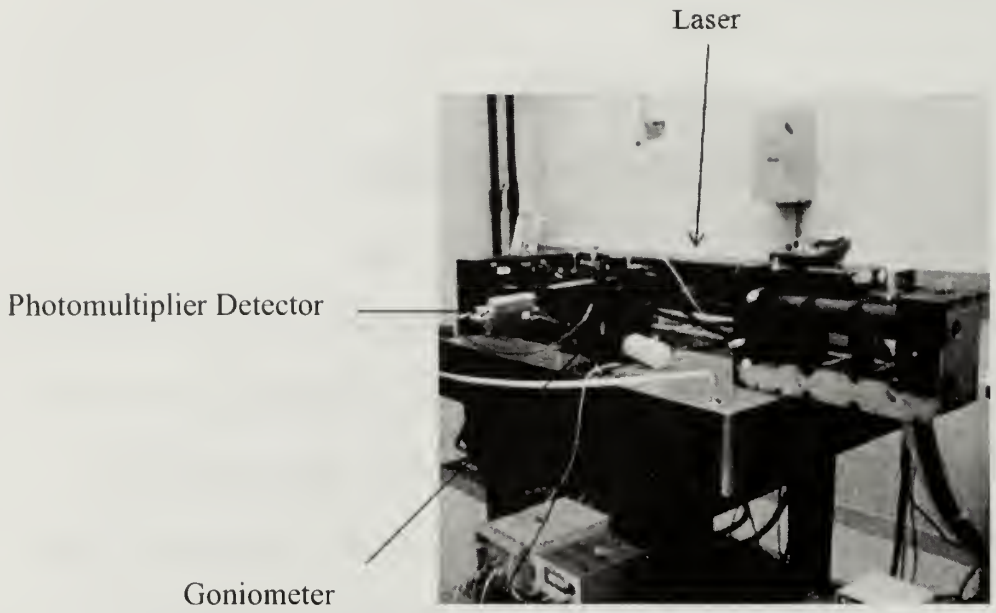

Figure 6.1 Light scattering set-up.

For polymers/particles larger than about $\lambda_0/20$ where λ_0 is the wavelength of the laser, intramolecular interference of scattered light becomes important. This leads to a dependence of the scattering intensity on the angle between the incoming laser beam and the sample detector axis. This effect is described by introducing into the scattering equation the form factor P (q) [3]

$$\frac{K \cdot c_2}{R(\theta)} = \left(\frac{1}{M_2} + 2A_2 c_2 + 3A_3 c_2 + \ldots \right) \cdot P(q)$$

Equation 6.1 General light scattering equation[1].

The scattering vector q is defined as

$$q = \frac{4 \cdot \pi \cdot n}{\lambda_0} \sin\left(\frac{\theta}{2}\right)$$

n = refractive index of medium
θ = scattering angle

Equation 6.2 Scattering vector q[1].

From P (q), information about particle size in solution can be obtained. The braced terms in equation 6.1 allow for interference of scattered light, an effect that makes the normalized scattered intensity concentration dependent. Incorporating intra-and inter-molecular interference corrections, and making a small angle approximation in the former, yield the Zimm equation

$$\frac{K \cdot c_2}{R(\theta)} = \frac{1}{M_2}\left(1 + \frac{R_g^2 \cdot q^2}{3}\right) + 2A_2 c_2 + \ldots,$$

Equation 6.3 General Zimm equation[1].

A plot of the left side versus $q^2 + kc_2$, where k is an arbitrary constant, followed by extrapolation to $c_2 = 0$ and $q^2 = 0$ gives M_w, A_2 and R_g^4, as shown graphically below.

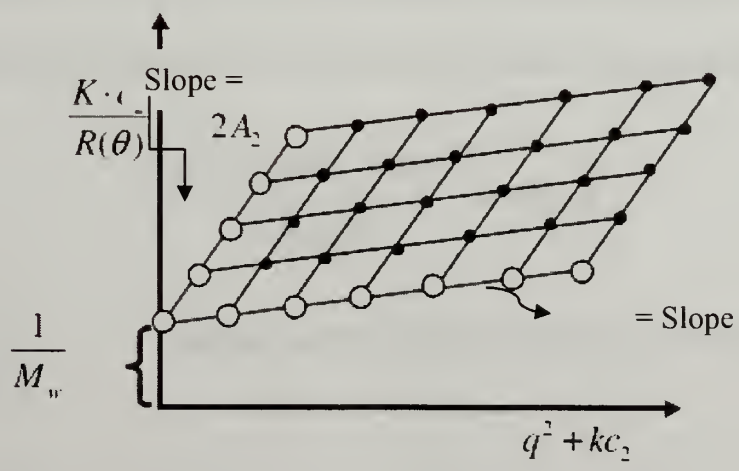

Figure 6.2 Zimm plot for M_w, A_2 and R_g determination.

Dynamic light scattering provides information on Brownian motion or diffusion processes of particles in solution. This information is obtained by analyzing fluctuations of the scattered light intensity. These fluctuations are dominated by local concentration changes in the solution. Solvent density fluctuations, also present, are usually so fast that they do not interfere with polymer diffusion coefficient measurement.

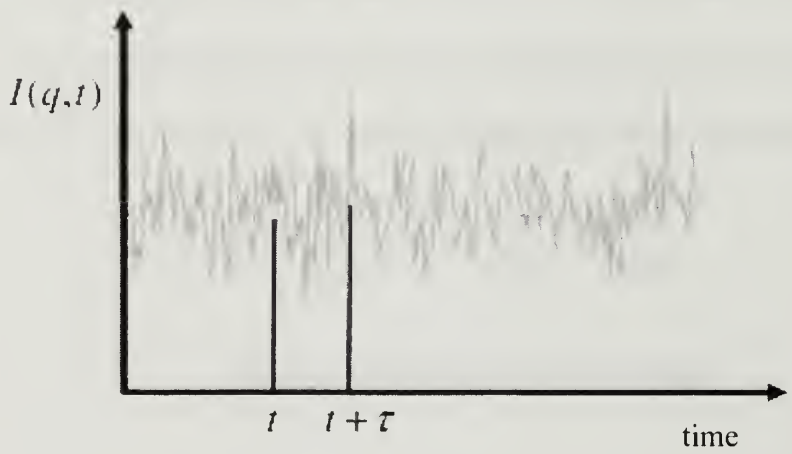

Figure 6.3 Intensity as a function of time.

Figure 6.3 shows a typical intensity as a function of time at one angle. From this measured function the normalized intensity autocorrelation function g_2 (τ) can be calculated.

$$g_2(\tau) = \frac{\langle I(q,t) \cdot I(q,t+\tau) \rangle_t}{\langle I(q) \rangle_t^2}.$$

Equation 6.4 Intensity autocorrelation function[1].

Where τ is the time interval and I (q, t) is intensity at time t. This function assesses the predictability of I (q, t+τ) based the value of I (q, t), and for τ approaching zero, I (q, t+τ) approaches 1. For large τ, g_2 (τ) approaches zero as I (q, t+τ) loses any connection to I (q, t), i.e., correlation in intensity is lost. Expected behavior is depicted in figure 6.4.

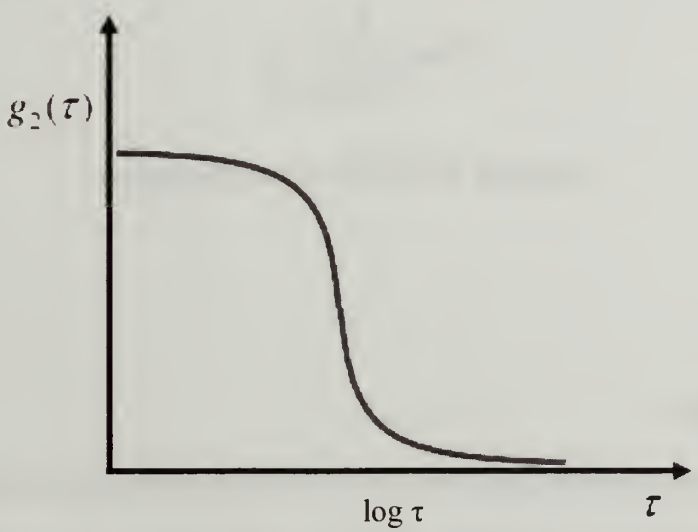

Figure 6.4 Intensity autocorrelation function.

In the case of dilute solutions, the normalized electric field auto correlation function g_1 (τ) can be related to changes in solute position with time.

$$g_1(q,\tau) = \frac{1}{N}\sum_{i=1}^{N}\left\langle \exp\left(-i\vec{q}\left[\vec{r}_i(0) - \vec{r}_i(\tau)\right]\right)\right\rangle$$

Equation 6.6 Amplitude autocorrelation function[1].

The exponential term manifests the statistics of polymer/particle displacement in a time span τ. For diffusive displacements, g_1 (q, τ) = exp (-Dq^2 τ). Thus, a plot of ln [g_1 (q, τ)] versus τ provides a straight line with the slope = -D q^2 from which the diffusion coefficient could be

determined. The measured quantity, $g_2(\tau)$, is related to the theoretical quantity $g_1(\tau)$, by the Siegert relation. For all solutes, the diffusion coefficient is related to the hydrodynamic radius R_h by the Stokes-Einstein equation, where k_B is the Boltzmann's constant, T is temperature and η is viscosity.

$$D = \frac{k_B \cdot T}{6\pi \cdot \eta \cdot R_h}$$

Equation 6.7 Stokes-Einstein equation[1].

Experimental Section

Light scattering experiments were performed at room temperature using an ALV unit equipped with an ALV/Sp125 precision goniometer (ALV-Laser Vertriebsgessellschaft m.b.h.), an Innova 70 argon laser (λ = 514.5 nm, max. power 3W, CoherentInc.) operated at 300 mW, and a photomultiplier detector (Thorn EMI Electron Tubes) (figure 6.1). Signal from the detector was processed by an ALV 5000 Multiple Tau Digital Correlator board and associated software. Milli-Q water was used to dissolve all samples unless otherwise stated. A typical sample preparation was as follows: 25 mg of sample was placed in a 25 mL scintillation vial and 5 mL of Milli-Q water was added. The vial was then placed in a low power sonicator for 10 minutes. The solution was next filtered (0.22 μm filter) into a 10x75 mm test tube, and the filtered solution was finally placed into the light scattering instrument. All light scattering experiments were performed under salt-free conditions.

Results and Discussion

Table 6.1. Static and Dynamic light scattering results for selected samples.

Polymer	dn/dc mL/g	M_w kDa	$M_{n\ calculated}$ kDa	$A_2 \cdot 10^{-7}$ mol cm^3 / g^2	R_g nm	R_h nm
PolyNorb-DiPEG	0.13	57	46	-5.62	24	9
PolyOxo-Norb-Diamine	0.1	70	60	9.79	15.2	8
PolyNorb-Diacid	0.1	40	50	2.65	41.6	9

Table 6.1 lists light scattering data for three selected homopolymers. The refractive index increment for each polymer was obtained using the refractometer signal of a GPC-MALLS system (Wyatt Technology). For the diPEG, system the weight average molecular weight M_w determined from static light scattering, 57 kDa, shows that this polymer is molecularly dissolved. The calculated number average molecular weight M_n for this molecule, 46 kDa, along with the measured polydispersity index, 1.17, gives a $M_{w,\ calculated}$ around 52 kDa, which is in good agreement. The value obtained for the second virial coefficient, is close to zero revealing that water is essentially a theta solvent for this polymer. Figure 6.5 shows dynamic light scattering results for this polymer. The spectrum shows a single peak at ~ 9 nm, which indicates no aggregation and single solvated polymer chains, which is in agreement with the static light scattering data.

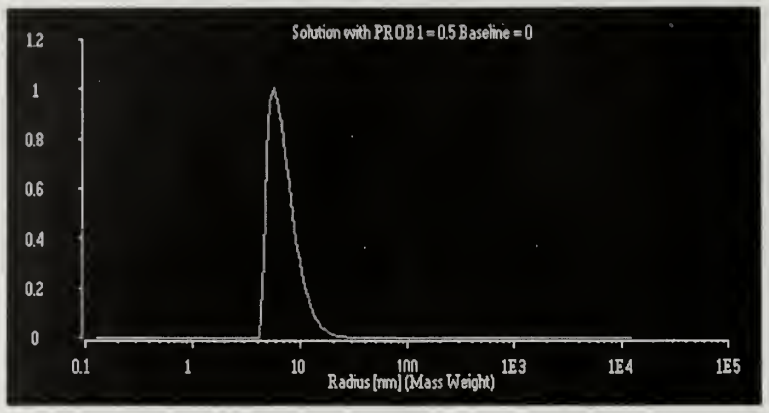

Figure 6.5 Dynamic light scattering results for polyNorb-DiPEG, R_h = 9nm.

For the diamine-containing polymers, A_2 is again close to zero, so thus, we can conclude that water is a theta solvent. From the PDI of 1.07 measured for these polymers, a M_w of ~ 64 kDa is derived from the calculated value of M_n a value in excellent agreement with the static light scattering result. This agreement again demonstrates that these polymers exist in solution as single chains. This is further confirmed by figure 6.6 which shows dynamic light scattering data for PolyOxo-Norb-Diamine.

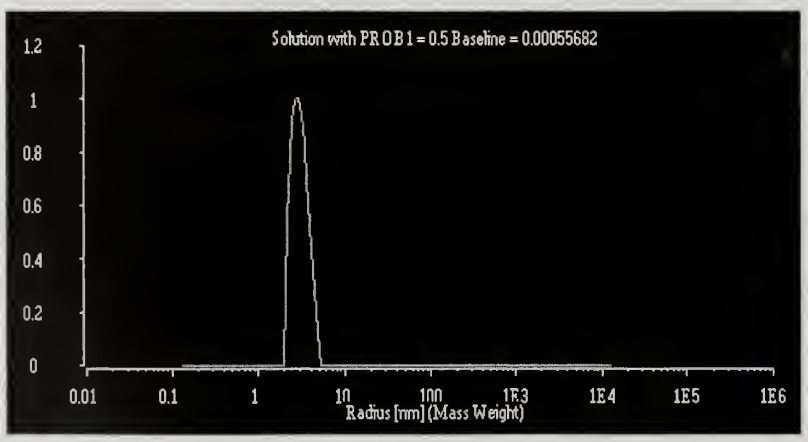

Figure 6.6 Dynamic light scattering results for PolyOxo-Norb-Diamine, R_h = 8nm

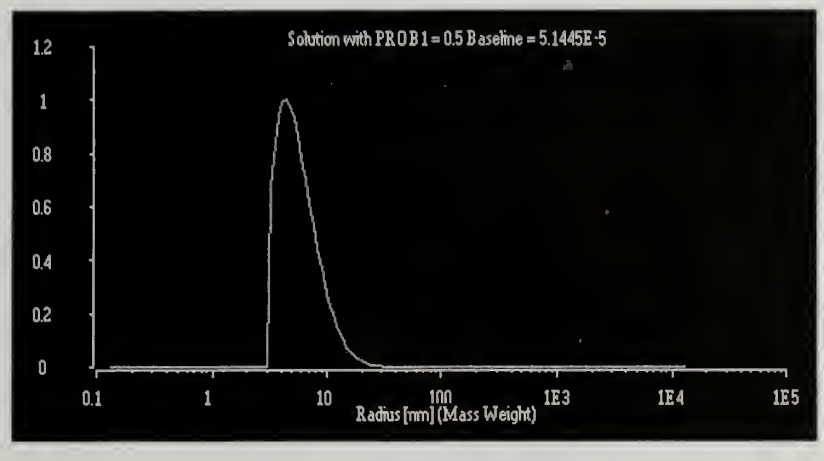

Figure 6.7 Dynamic light scattering results for polyNorb-Diacid, R_h = 9nm

From static light scattering, a Mw of 70 kDa was obtained. With a measured PDI of 1.06 a number average molecular weight of 66 kDa is obtained. This number is in agreement with the theoretical value of 50 kDa. Figure 6.7 shows DLS data obtained for polynorb-Diacid. This data indicates that the polymers are molecularly dissolved with no aggregated structures detected. From light scattering a M_w of 40 kDa was obtained for diacid polymers. With an obtained PDI of 1.06 a theoretical number average molecular weight of 38 kDa was calculated. This value is in good agreement with 50 kDa $M_{n,\ calculated}$. The second virial coefficient obtained for these polymers is also small and close to zero indicating that water is a theta solvent for these polymers.

So far we have demonstrated that ROMP is amenable to the synthesis of well defined polymers. These polymers have been shown to exist in solution as solvated molecules although, is at best, a theta solvent. For the block copolymer systems, MW and absolute A_2 values were not measured, and scattered light intensity between 30 - 120° was lower than the measured intensity for pure water, hence reliable results could not be obtained. However, qualitative arguments can

be made for their existence as unimers in solution. For the DiPEG- Diacid block copolymers, each block was shown to exist as single chains. It seems highly unlikely that a diblock consisting of these two monomers would dissolve in water to form small aggregates. It has been shown, however, that block copolymers consisting of PEO and acrylic acid associate in aqueous solution[5]. These associations are believed to result from hydrogen bonding and hydrophobic interactions. Additionally, Ikawa and coworkers have demonstrated that the critical precipitation pH for mixed solutions of linear PEO/PAA homopolymers is 1.9[6].

Our polyacid polymers dissolve in water to form solutions with a pH of 2.6 at a concentration of 5mg/mL This implies that solutions containing poly (norb-diacid-*b*-norb-diPEG) do not aggregate in water due to a pH value higher than the reported critical precipitation value for poly (acrylic acid). Further experiments will have to be performed to confirm the above hypothesis since poly (acrylic acid) contains only one carboxylic acid group per repeat unit. Also, the backbone for our systems is more hydrophobic than poly (acrylic acid). It is possible that acid catalyzed hydrolysis of the ester bond connecting the PEG side groups to the polymer backbone could occur. However, the time scale for this to occur is far greater than the DLS experiment time. Additionally figure 6.8 shows typical DLS data obtained for block copolymers consisting of these two monomers at a concentration of $3mgL^{-1}$.

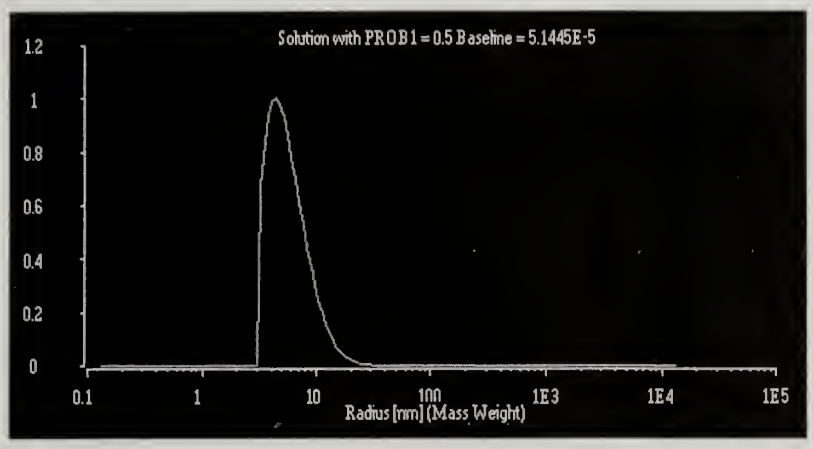

Figure 6.8 Dynamic light scattering results for poly (Norb-Diacid-*b*-Norb-DiPEG), R_h = 7nm M_n = 27 kDa 1.06

results indicate that this diblock exists in solution as single solvated chains; however, the extremely small value for the hydrodynamic radius is perplexing. It is possible that the diblock exists as stable collapsed chains and hence give very small values for their hydrodynamic radius. The values obtained as also very close to lower limit measurable by the instrument; hence this value is inherently very inaccurate. Qualitative data of the scattered light intensity divided by concentration versus concentration at low concentrations was plotted (figure 6.9). This qualitative slice of a Zimm plot at one angle gave a positive slope. The slope of this plot gives the second virial coefficient which indicates that water is a good solvent for this copolymer system.

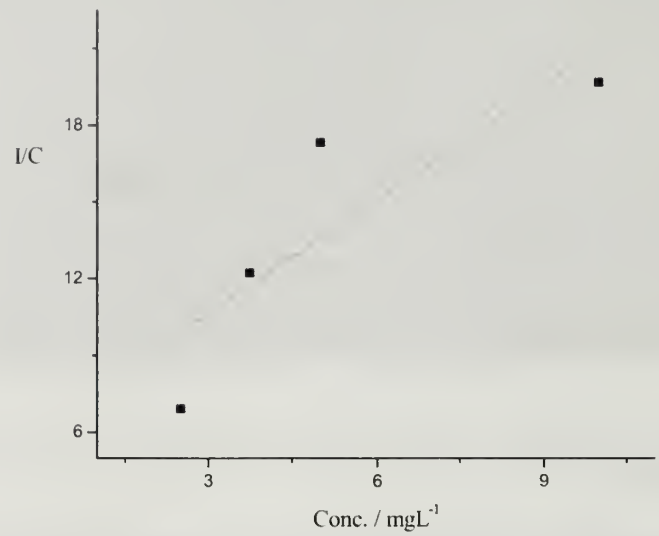

Figure 6.9 Intensity/concentration vs. concentration for poly (Norb-Diacid-*b*-Norb-DiPEG), M_n = 27 kDa 1.06

For the diblock copolymers consisting of Oxo-Norb-Diamine and Norb-DiPEG, the situation is similar but a bit clearer. Figure 6.10 shows DLS data obtained for one of these copolymers at 3mgL^{-1}. Single chains with a hydrodynamic radius of 5.2 nm are obtained which gives an indication that the diblocks are molecularly dissolved with no aggregated structures observed.

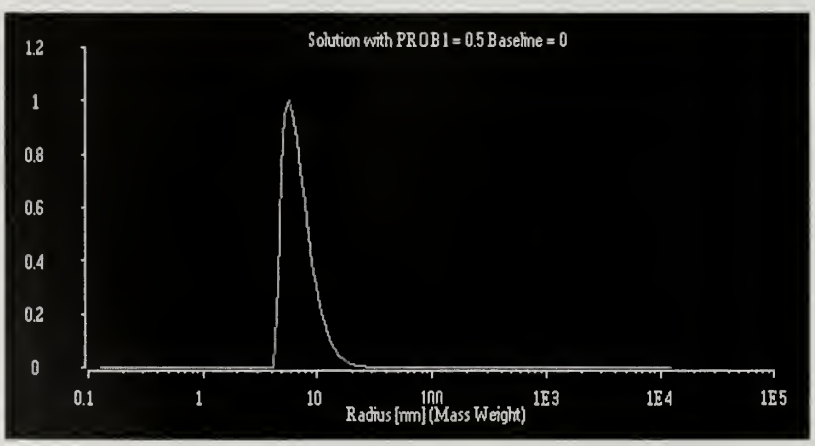

Figure 6.10 DLS data for poly (Oxo-Norb-Diamine-*b*-Norb-DiPEG), R_h = 5.2nm M_n = 49k kDa 1.07

A plot of intensity divided by concentration versus concentration (figure 6.11) also gives a positive slope which shows that water is either a good or theta solvent for these polymers.

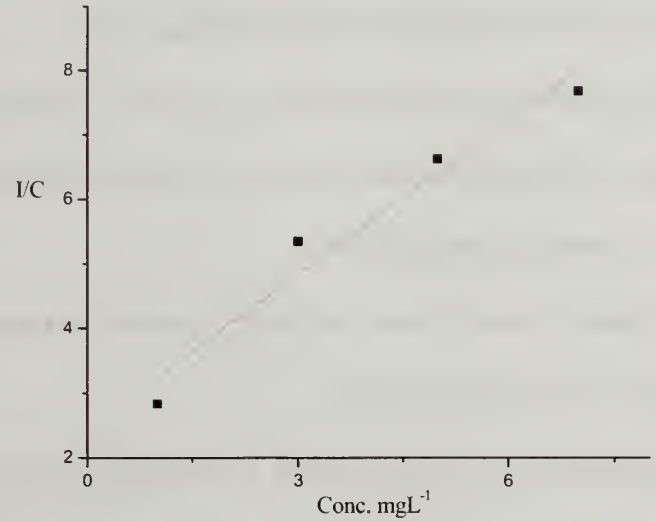

Figure 6.11 Intensity/concentration vs. concentration for poly (Oxo-Norb-Diamine-*b*-Norb-DiPEG), M_n = 49 kDa 1.07

Dynamic and static light scattering was used to confirm the water the apparent dissolution of homopolymers synthesized in chapters 2 through 4. These experiments gave small positive second virial coefficients for both of the ionic homopolymers and a small negative coefficient for poly (norb-DiPEG). Since this value close to zero it can be argued that water is a good solvent for this polymer. These results indicate that our homopolymers are molecularly dissolved. For our diblock copolymer systems a non-rigorous argument implies that these polymers also exist in water as single chains. This argument is supported by DLS which shows single peaks below 10 nm for both block copolymers. So far we have demonstrated that we can synthesize homopolymers and block copolymers that are water soluble. This property was utilized to synthesize superabsorbent gels. Their synthesis and solution properties are detailed in the following chapter.

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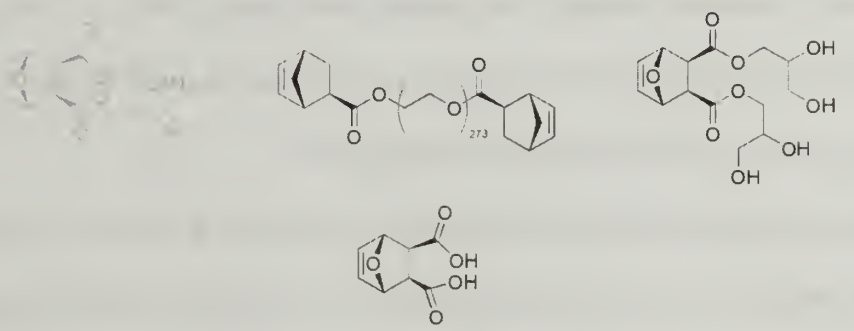
CHAPTER 7

SUPERABSORBANT POLYMER GELS



Introduction

One of the most fulfilling accomplishments of any scientist is a breakthrough or theory that has the potential to positively impact human lives. During our work to synthesize WSPs, we discovered crosslinked polymer systems that could absorb many times their weight in water. The process to synthesize these materials is fast, and the properties of the resulting superabsorbent polymers (SAPs) can be tuned easily by manipulating the ratio of monomer to catalyst, changing the side groups on the monomer units, using two or more monomers in the feed, or changing the crosslink density.

Superabsorbent polymers are primarily used as absorbents for water and aqueous solutions in diapers, adult incontinence products, feminine hygiene products, and similar applications. Early superabsorbent materials were crosslinked starch-g-polyacrylate polymers[1]. Polyacrylic acid and its sodium or potassium salts eventually replaced earlier SAPs, and polyacrylic acid is the primary polymer employed for superabsorbent polymers today polymer. Superabsorbent polymers typically absorb, and retain under a slight mechanical pressure, about 30 - 1000 times their weight in water[2-4]. The swollen gel holds the liquid in a solid, rubbery state, preventing the liquid from leaking.

To emphasize the importance and growth of the superabsorbent industry, the following statistic was released by the company Global Industry Analysts, Inc.: "Global Super-Absorbent Polymers market is projected to reach 1.49 million metric tons by 2010....." Presently, Global demand for SAP is estimated at 1.05 million tons. Clearly this is a very dynamic and developing industry with a high impact in various areas of human life.

Most commercial superabsorbent polymers are prepared from acrylic acid and a crosslinker by solution or suspension polymerization. The type and quantity of crosslinker control both the swelling capacity and gel modulus. The synthesis and use of crosslinked polyacrylate superabsorbent polymers have been a popular topic in the polymer literature. However, little information about manufacturing processes has been given due to its proprietary content. Most SAPs synthesized today are made via free radical polymerization[5-10]. With regard to other polymerization techniques, ROMP, in particular, there are surprisingly no reported examples. Our polymers represent the first example of SAPs made from the ROMP process. In this chapter, we detail the process of synthesizing these materials and quantify the amount of water absorbed.

Experimental Section

2, 2-Dimethyl-4-hydoxymethyl-1-3-dioxolan (97%) (solketal) was purchased from Fluka and used as received. Bicyclo [2.2.1] hept-5-ene-2-carboxylic acid, methyl ester was purchased from Sigma-Aldrich and used without further purification. Exo-3, 6-epoxy-1, 2, 3, 6-tetrahydrophthalic acid (99 %) was purchased from TCI and purified by precipitation from ether and dried for 12 hours prior to use. Polyethylene oxide containing hydroxyl end groups (PEG M_n = 12 kDa) was purchased from Fluka and heated at 120°C under nitrogen for 2 hours prior to

use. *N*, *N*-dicyclohexylcarbodiimide (DCC) (99%) was purchased from Fluka and used as received. 4-(Dimethylamino) pyridine (DMAP) (99%) was purchased from Sigma-Aldrich. *p*-Toluenesulfonic acid monohydrate (98.5 %) (PTSA) was purchased from Sigma-Aldrich. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under nitrogen prior to use. Anhydrous *N*, *N*-dimethylformamide (99%) (DMF) and anhydrous dichloromethane (99%) (DCM) were both purchased from Sigma-Aldrich and purged with nitrogen prior to use.

Synthesis of Monomers and Crosslinker. To a 100 mL round bottom flask was added 7g (0.042 mol) of *exo* 7-Oxabicyclo [2.2.1] hept-5-ene-2, 3-dicarboxylic anhydride, 0.30 g (0.008 mol) of DMAP, 0.3 (0.008 mol) of PTSA, 11.14 g (0.084 mol) of solketal and 50 mL of acetone. This mixture was stirred under nitrogen for 12 hours after which the solvent was removed. Approximately, 50 mL of DCM was then added and the resulting solution cooled to 0°C. 8.6 g (0.042 mol) of DCC in 15 mL DCM was then added drop-wise over 1 hour. This reaction was left for an additional 3 hours. The resulting white precipitate was filtered off and the filtrate concentrated. The crude product (oxo-norb-tetrasolketal) was purified by precipitation from hexane: ether (5: 1) to give 14.7 g (yield = 85 %) of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (s, 6H), 1.45 (s, 6H), 2.88 (s, 2H), 3.75 (m, 2H) , 4.07-4.35 (m, 8H), 5.29 (s, 2H), 6.48 (s, 2H). (see figure 7.1).

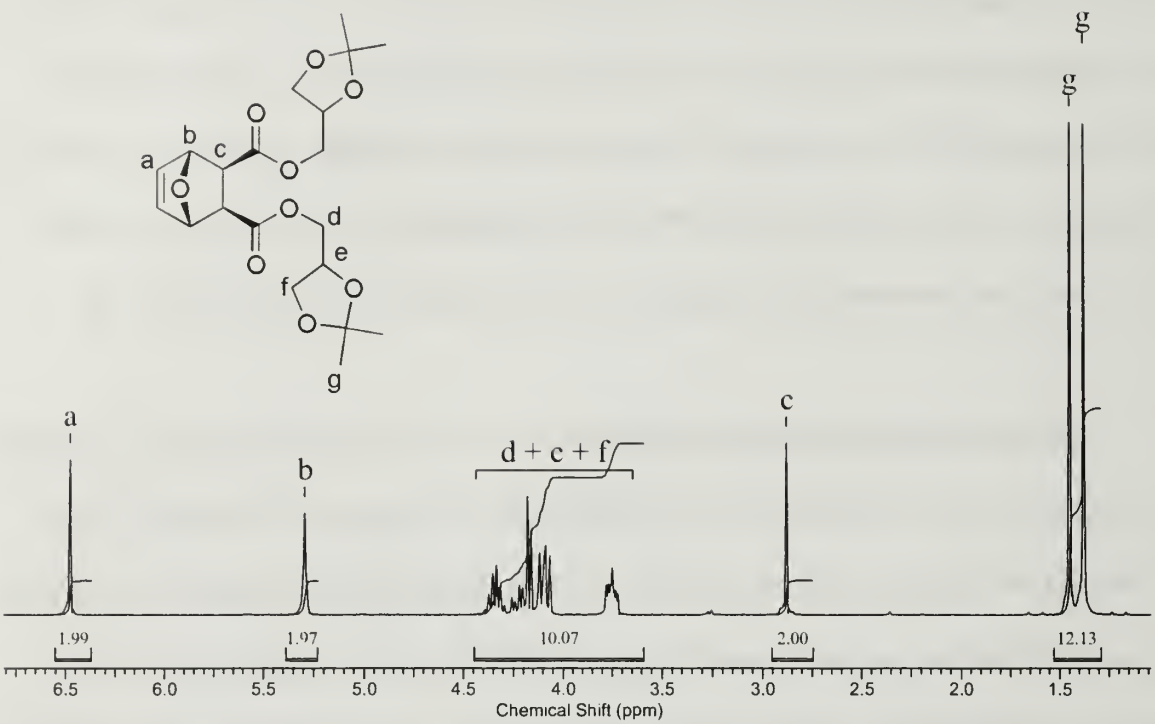


Figure 7.1 ^{1}H NMR spectrum of oxo-norb-tetrasolketal in $DMSO_6$.

4 g (0.0097 mol) of this product was dissolved in 5 mL THF. To this solution was added a few drops of HCl and the reaction left for 2 hours. Proton NMR of the crude product showed 100 % deprotection of the hydroxyl groups. The hydroxyl functionalized oxo-norbornene was then purified by gradient chromatography using ether: ethanol (0-100 %) to give ~ 2.7 g (recovered yield = 90 %) of a clear viscous oil.

^{1}H NMR (300 MHz, $DMSO_6$) δ 2.82 (s, 2H), 3.17 (s, 1H), 3.33 (d, J= 3Hz, 4H), 3.62 (t, J= 3Hz, 4H), 3.76 (q, J=6Hz, 2H), 3.921(d, J= 6Hz), 4.06 (dd, J= 3Hz, 2H), 5.13 (s, 2H), 6.48 (s, 2H). ^{13}C NMR (75 MHz, $DMSO_6$) δ 25.39, 26.75, 46.85, 65.65, 66.34, 73.49, 80.70, 109.88, 136.68, 171.27. IR cm^{-1} 1916, 1192, 1733, 2984, 2950, 3338. Scheme 7.1 summarizes the synthesis of this monomer.

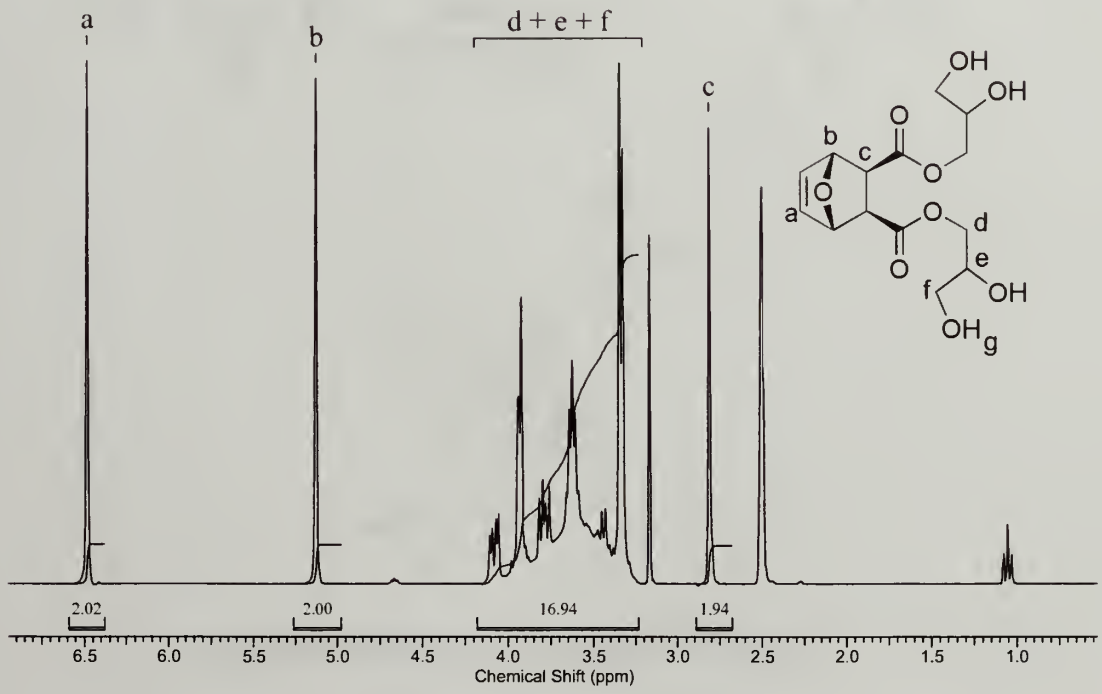
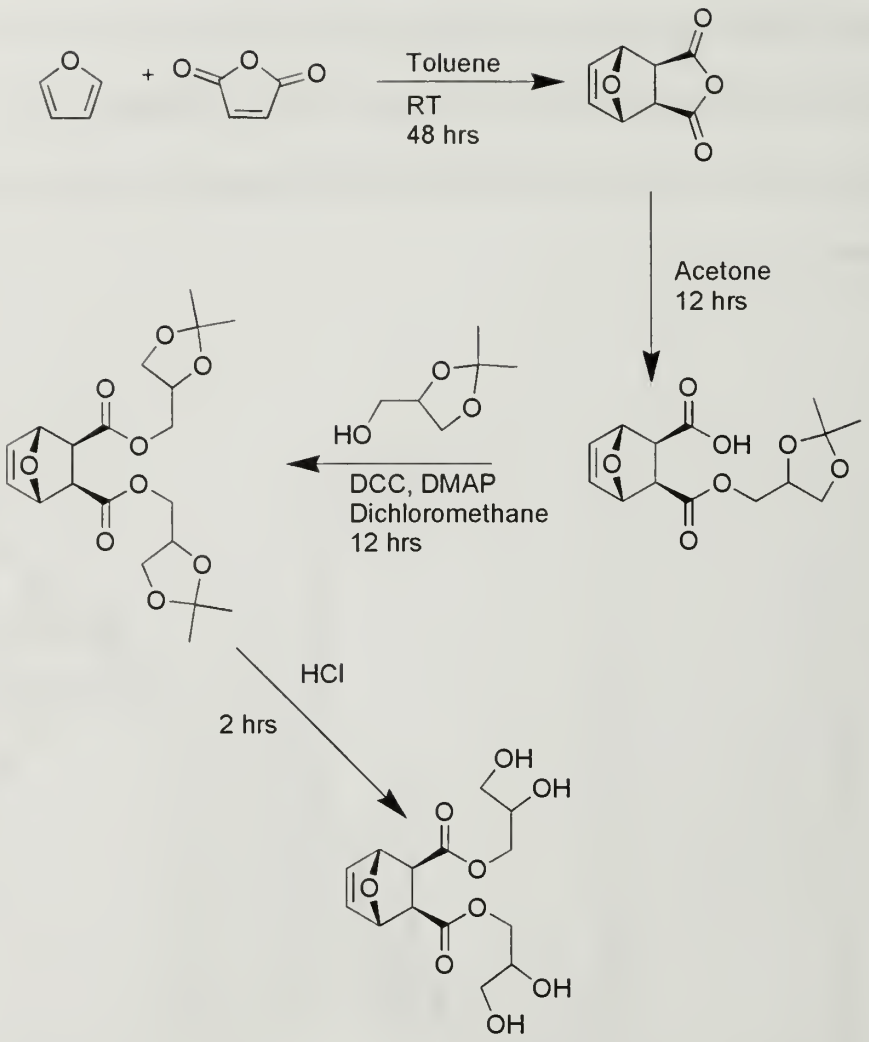
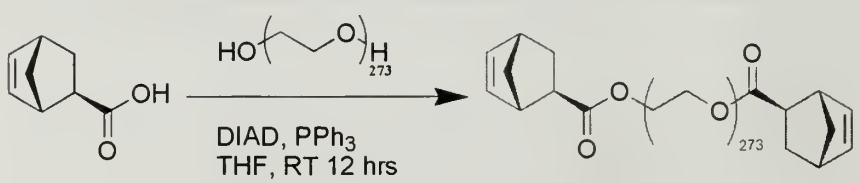


Figure 7.2 ^{1}H NMR spectrum of oxo-norb-tetrahydroxy in $DMSO_6$.



Scheme 7.1 Synthesis of Oxo-Norb-Tetrahydroxy.



Scheme 7.2 Synthesis of 12 kDa PEG crosslinker.

Scheme 7.2 shows the synthesis for the crosslinker used in this study. This crosslinker was chosen based on a desire to obtain gels that would absorb many times their weight of water. Initial experiments to crosslink polymers from oxo-norb-diacid using dicyclopentadiene were also successful. However, the swelling ratio for these gels were typically small (1 g of gel would absorb 1 g of water). Thus, in order to increase the swelling ratio of these gels, we decided to incorporate a crosslinker that was water soluble. We utilized earlier synthetic methodologies to synthesize a PEO (M_n = 1100) based crosslinker end-capped with norbornene anhydride groups. Polymerizations were rather slow and the resulting gels did not absorb much water. We turned to the mono acid norbornene with hopes we could get faster reaction times. This did indeed occur and we were able to obtain modest swelling ratios (1g of gel to 5 g water). Motivated with this success we endeavored to improve upon the swelling ratio and decided to incorporate an even longer PEO spacer, as presented in this chapter.

The monoacid was synthesized according to a literature procedure[11]. 25 mL (0.304 mmol) of cyclopentadiene and 30.1 mL (0.335 mmol) of methyl acrylate were dissolved in 30 mL of DCM and refluxed for 24 hours. The solvent was then removed and the resulting crude product dissolved in sodium methoxide solution and refluxed again for 4 hours. The solvent was then removed and 50 mL of water added and refluxed for 12 hours. The solution was made basic and washed with ether to remove any residual cyclopentadiene. The solution was then acidified and the product extracted with diethyl ether and dried over magnesium sulfate. The *exo* isomer was obtained from the mixture by iodolactonization. The isomers were dissolved in sodium bicarbonate solution and a solution of iodine and potassium iodide was added drop wise. The aqueous layer was washed with diethyl ether to remove iodolactone. The colored solution was decolorized by addition of sodium thiosulfate solution. The aqueous solution was then acidified

to pH = 2 by the slow addition of sulfuric acid. The resulting product was then extracted from the mixture with diethyl ether and dried over magnesium sulfate. The acid was further purified by precipitation from cold pentane to provide 7.84g (yield = 43%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35-1.42 (m, 2H), 1.52 (d, J= 10Hz, 1H), 1.93 (t, J = 4, 12 Hz, 1H), 2.27-2.22 (m, 1H), 2.92 (bs, 1H), 3.09 (bs, 1H), 6.15-6.11 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.3, 41.6, 43.2, 46.4, 46.7, 135.7, 138.1, 182.9.

0.4g (2.8mmol) of the mono acid product, 10 g (833μmol) of 12kDa PEG, and 1g (3.8mmol) triphenylphosphine was placed in a 50 mL round bottom flask. This solution was cooled to 0°C then 1 mL (4.9mmol) DIAD was added drop wise. The reaction was left for 12 hours after which the solution was added to 500 mL of diethyl ether. The white precipitate was then filtered and washed with cold hexane. This process was repeated two more times. The crosslinker was then dried under vacuum for 24 hours to give 7g (~70% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (m, 2H), 1.38 (m, 2H), 1.52 (d, J= 10Hz, 1H), 2.93 (m, 1H), 3.05 (m, 1H), 3.41 (m, 4H), 3.89 (m, 5H), 4.25 (m, 1H), 6.15 (m, 2H).

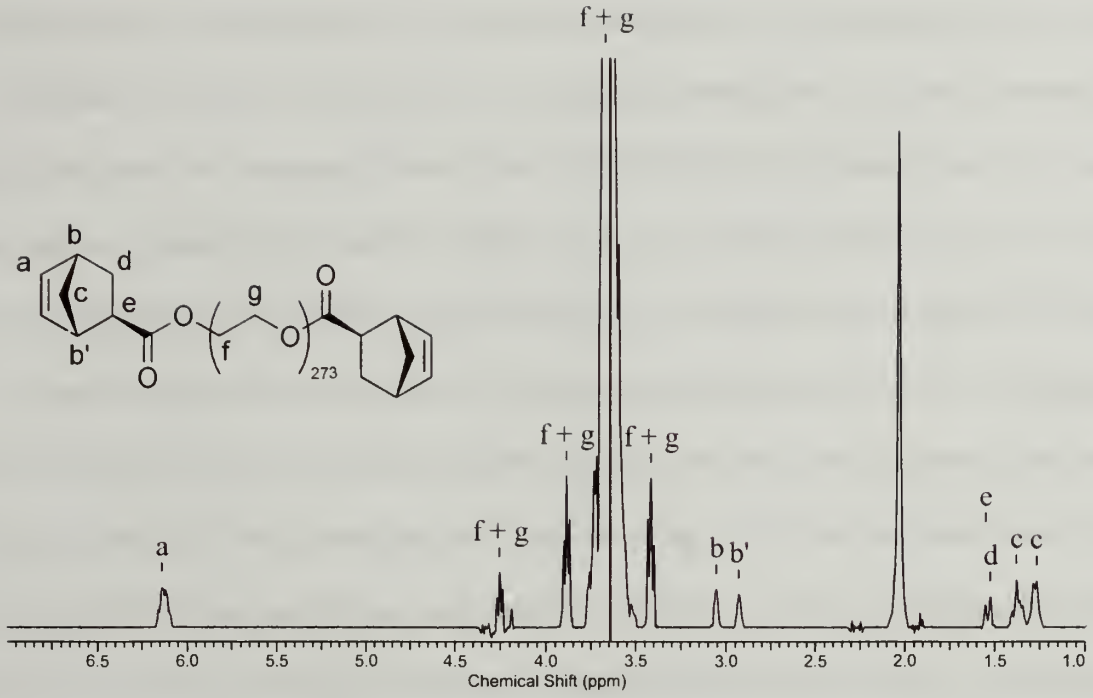
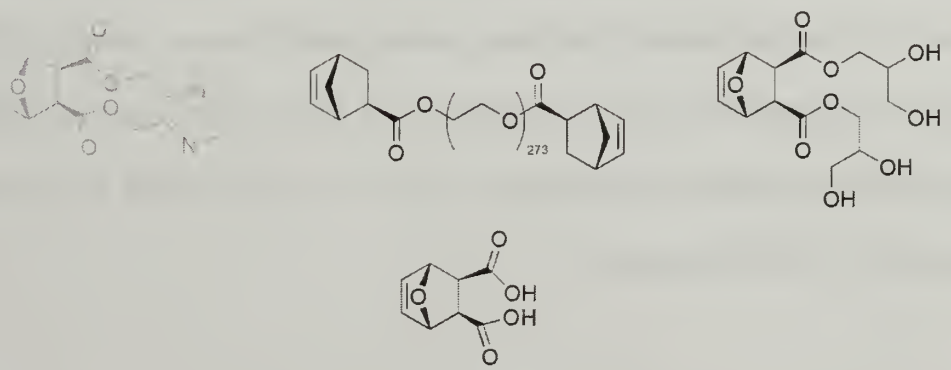


Figure 7.3 ^{1}H NMR spectrum of 12kDa crosslinker in $CDCl_3$.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added a predetermined amount of crosslinker equivalent to 1 mole percent of added monomer. To a separate 25 mL vial, an appropriate amount of G3 was added to theoretically obtain a degree of polymerization of 100. THF (DMF for the hydroxyl monomer) was then added to each vial, the monomer solution added quickly to the catalyst solution. This solution was then added quickly to a Teflon well plate (figure 7.5) placed in a large cylindrical bowl (reaction chamber) containing THF. The Teflon plate was covered with a glass slide and the reaction chamber covered with aluminum foil. After one hour, the Teflon plate was removed and the gel air dried for a period of time required for the gel to separate from the plate. After separation, the gel was placed in a soxhlet with acetone as solvent (methanol was used for the diacid and tetrahydroxy monomers) for 12 hours to remove any unreacted monomer, crosslinker and/or sol fraction. The soxhleted gel was then dried in a vacuum oven at 40°C for 12 hours. The dried gel was then swollen in water (500 mL) with different pH values (4.5, 8.5) and a 0.9wt % salt solution. The gel was left for 12 hours to reach equilibrium and then removed and weighed. The swollen gel was placed in a Buchner funnel fitted with a porous plastic film and allowed to "drain". The wet gel was then weighted using a plastic weighting boat. The amount of water was then calculated using the following equation: Swelling ratio = $[W_i - W_o] / W_o$[12], where W_i is the weight of the wet gel, and W_o is the dry gel mass .

Figure 7.5 Teflon well plate containing oxo-norb-diamine dry gels.

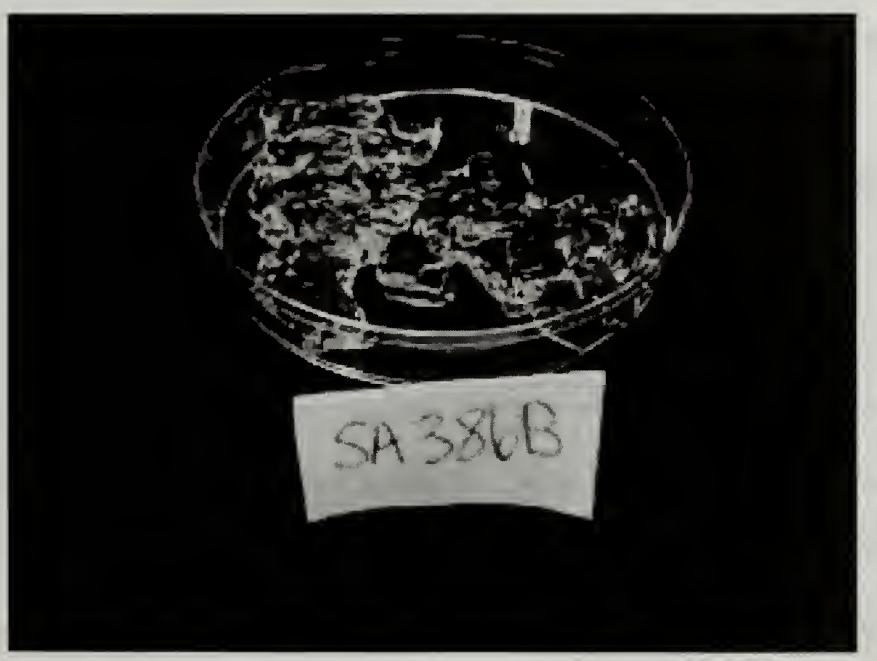

Figure 7.6 Wet gel obtained from oxo-norb-diamine and 0.4 mol% crosslinker at pH 4.5.

Figure 7.7 Wet gel obtained from oxo-norb-diacid and 5 mol% crosslinker at pH 4.5.

Results and Discussion

Tables 7.1-7.3 summarize swelling data obtained for oxo-norb-diamine. The tables show an inverse relationship between swelling ratio and mol % of crosslinker. A higher crosslink density translates into a stronger network that is not able to expand as much as a more lightly crosslinked network. Qualitative evidence for network strength as a function of mol % crosslinker can be seen by observing the stiffness of the wet gels in each series. Gels with 10 mol % crosslinker are stiff and can be readily held with a pair of tweezers without breaking. As the mol % of crosslinker is decreased, the gels become softer and more difficult to handle. The swelling of these gels can be explained in terms of an ionic swelling pressure generated by the difference in osmotic pressure between mobile counterions within the gel and in the outer solution[13]. Swelling occurs until the osmotic pressures inside the gel and in the outer solution are equal. A commercially

available sample of lightly crosslinked polyacrylic acid used in diapers was subjected to the same swelling ratio determination conditions as our gels. Swelling ratios of 379, 468 and 40 were obtained in water at pH 8.5, 4.5 and 0.9 wt% NaCl respectively. Our gels at pH 4.5 and 0.4 mol % crosslinker had swelling ratios of 334, 575 and 53. These results are promising, and it should be noted that the mol % of crosslinker in the polyacrylic acid samples was not known; they could be much lower than our values.

Table 7.1. Gel Data for oxo-norb-diamine. [a] Swelling determined for water at pH 8.5

Mass of Monomer/ mg	Mol% Crosslinker	Mass Crosslinker / mg	Mass of G3 / mg	Gel Dry Mass / mg	Gel Wet Mass / mg	[a]Swelling Ratio
50	0.4	7	1.3	41	13756	**334**
50	0.6	11	1.3	49	11340	**230**
50	0.8	14	1.3	53	7301	**138**
50	1	18	1.3	56	4812	**85**
50	2	36	1.3	65	2509	**38**
50	5	90	1.3	108	2280	**20**
50	10	180	1.3	161	2581	**15**

Table 7.2. Gel Data for oxo-norb-diamine. [b] Swelling determined for water at pH 4.5

Mass of Monomer/ mg	Mol% Crosslinker	Mass Crosslinker / mg	Mass of G3 / mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[b]Swelling Ratio
50	0.4	7	1.3	48	27640	**575**
50	0.6	11	1.3	44	18908	**429**
50	0.8	14	1.3	44	11954	**270**
50	1	18	1.3	60	12840	**213**
50	2	36	1.3	72	7419	**102**
50	5	90	1.3	128	6336	**49**
50	10	180	1.3	193	5719	**29**

Table 7.3. Gel Data for oxo-norb-diamine. [c] Swelling determined for water containing 0.9 wt%

Mass of Monomer/ mg	Mol% Crosslinker	Mass Crosslinker / mg	Mass of G3 / mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[c]Swelling Ratio
50	0.4	7	1.3	43	2281	**53**
50	0.6	11	1.3	43	2242	**52**
50	0.8	14	1.3	49	2268	**45**
50	1	18	1.3	47	2143	**44**
50	2	36	1.3	62	2138	**34**
50	5	90	1.3	103	2809	**26**
50	10	180	1.3	193	4300	**21**

Tables 7.4 – 7.6 show the swelling data for the diacid monomer. The values obtained show a similar trend to the amine samples with respect to mol % crosslinker and swelling ratio although the trends are not as pronounced as for the diamine. The reason for the much larger swelling obtained for the diamine compared to the diacid is unclear, as the swelling in ionic gels is controlled by the counterions surrounding each charged functional group. It is possible that at pH 8.5 our diacid gels are *less* ionized than the diamine gels at pH 4.5. This implies that more counterions are available in the diamine gels and hence a greater osmotic pressure is developed. The degree of dissociation for both gels is affected by the distance between functional groups. For the diacid gels the acid groups are close to each other and dissociation to yield a dianionic species is reduced due to charge repulsion. For the diamine gels the amine groups have more freedom and hence are further apart from each other. This distance negates charge-charge repulsion and these gels are able to ionize to a greater extent. The wet gels obtained from oxo-norb-diacid are all readily handled. At 10 mol % crosslinker, the gels have significant stiffness.

Table 7.4. Gel Data for oxo-norb-diacid. [d] Swelling determined for water at pH 8.5

Mass of Monomer/ mg	Mol% Crosslinker	Mass of Crosslinker / mg	Mass of G3/ mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[d]Swelling Ratio
50	1	32.4	2.4	27	503	**18**
50	2	64.8	2.4	37	343	**8**
50	5	162	2.4	69	886	**12**
50	10	324	2.4	93	1441	**15**

Table 7.5. Gel Data for oxo-norb-diacid. [e] Swelling determined for water at pH 4.5

Mass of Monomer/ mg	Mol% Crosslinker	Mass of Crosslinker / mg	Mass of G3/ mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[e]Swelling Ratio
50	1	32.4	2.4	27	106	**3**
50	2	64.8	2.4	35	161	**4**
50	5	162	2.4	70	625	**8**
50	10	324	2.4	81	1025	**12**

Table 7.6. Gel Data for oxo-norb-diacid. [f] Swelling determined for water containing 0.9 wt%

Mass of Monomer/ mg	Mol% Crosslinker	Mass of Crosslinker / mg	Mass of G3/ mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[f]Swelling Ratio
50	1	32.4	2.4	13	254	**19**
50	2	64.8	2.4	18	183	**9**
50	5	162	2.4	53	596	**10**
50	10	324	2.4	145	1698	**11**

Table 7.7 – 7.9 summaries the conditions and results obtained for gels made from Oxo-Norb-Tetrahydroxy. The swelling ratios are statistically the same indicating that the absorbency is not influenced by pH.

Table 7.7 Gel Data for oxo-norb-tetrahydroxy. [g] Swelling determined for water at pH 8.5.

Mass of Monomer/ mg	Mol% Crosslinker	Mass of Crosslinker / mg	Mass of G3/ mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[g] Swelling Ratio
50	1	19.4	1.4	22	471	**21**
50	2	38.8	1.4	10	192	**18**
50	5	97.0	1.4	10	144	**14**
50	10	194	1.4	56	820	**14**

Table 7.8 Gel Data for oxo-norb-tetrahydroxy. [h] Swelling determined for water at pH 4.5.

Mass of Monomer/ mg	Mol% Crosslinker	Mass of Crosslinker / mg	Mass of G3/ mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[h] Swelling Ratio
50	1	19.4	1.4	10	214	**20**
50	2	38.8	1.4	15	290	**19**
50	5	97.0	1.4	18	338	**18**
50	10	194	1.4	55	760	**13**

Table 7.9 Gel Data for oxo-norb-tetrahydroxy. [i] Swelling determined for water containing 0.9 wt% NaCl.

Mass of Monomer/ mg	Mol% Crosslinker	Mass of Crosslinker / mg	Mass of G3/ mg	Gel Dry Mass/ mg	Gel Wet Mass/ mg	[i] Swelling Ratio
50	1	19.4	1.4	14	288	**19**
50	2	38.8	1.4	8	130	**15**
50	5	97.0	1.4	20	364	**17**
50	10	194	1.4	60	748	**12**

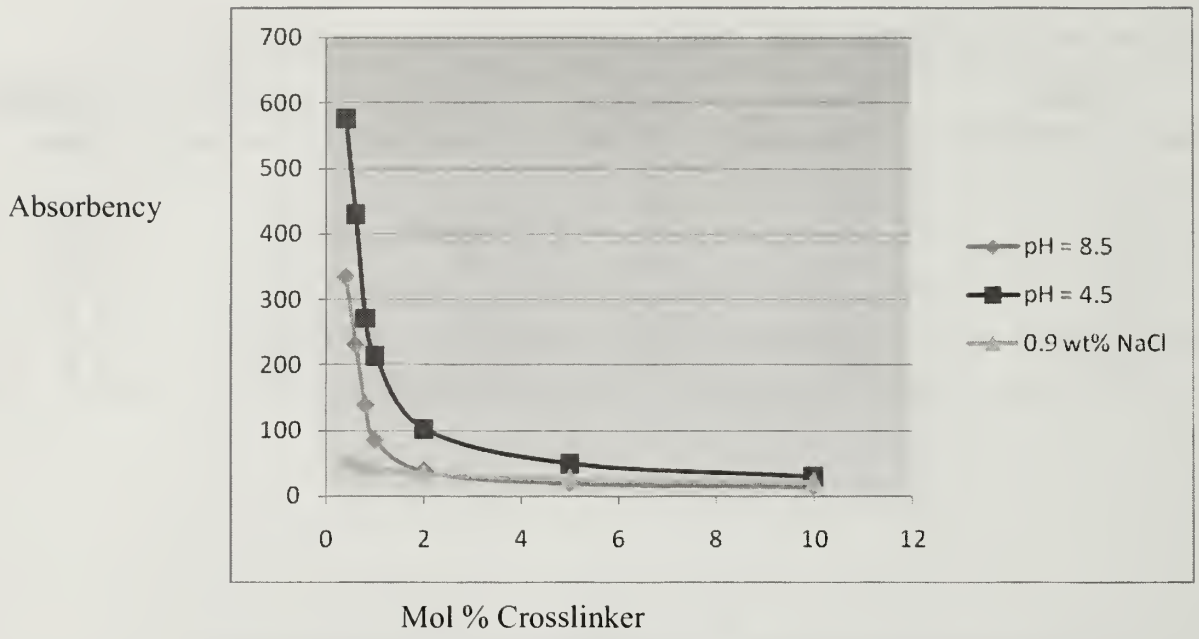

Figure 7.8 Graph summarizing swelling data for oxo-norb-diamine.

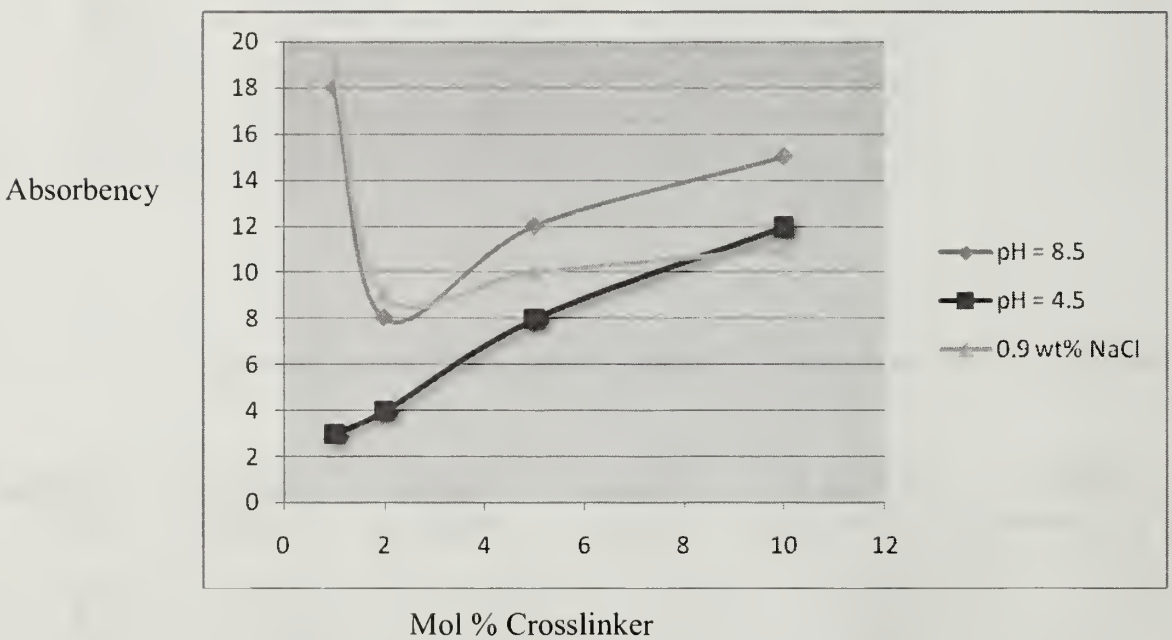

Figure 7.9 Graph summarizing swelling data for oxo-norb-diacid.

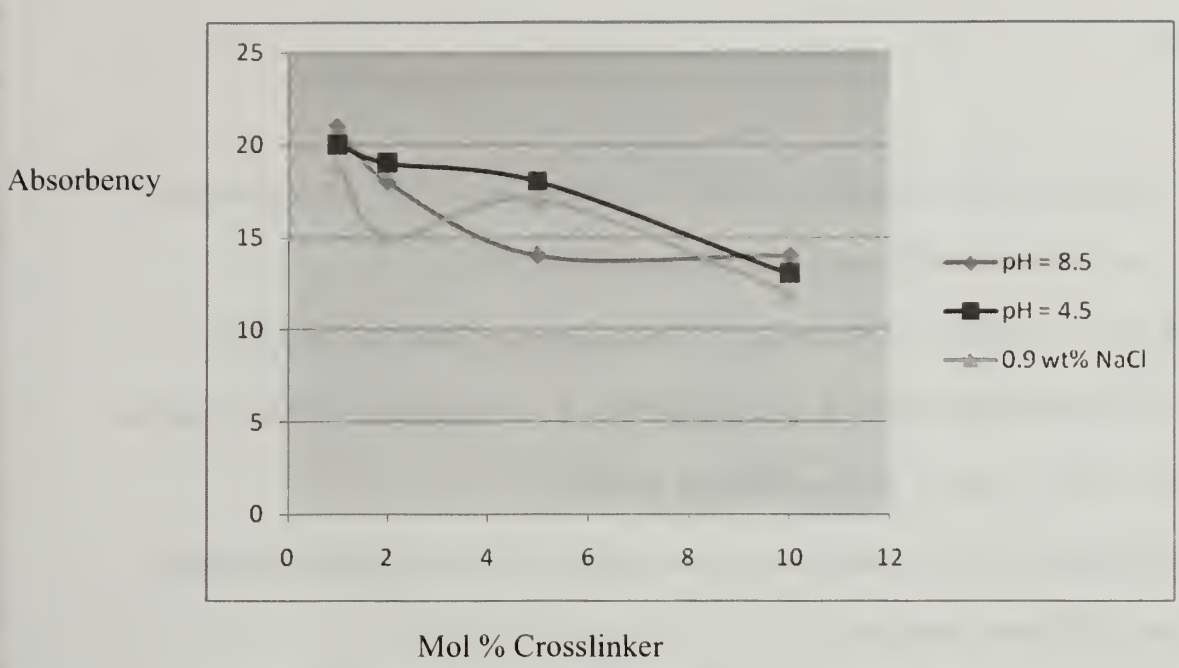

Figure 7.10 Graph summarizing swelling data for oxo-norb-tetrahydroxy.

Figures 7.8-7.10 summarize the swelling data obtained for all three monomers. It is evident that many factors contribute to the water absorbency of gels derived from these monomers. All factors are not well understood presently, and further work will be performed to substantiate some of the theories outlined above. A full understanding of the parameters that contribute to swelling ratio and gel modulus are not necessary to make qualitative observations that the gel forming process presented has great potential in the superabsorbant industry. In this chapter we presented an easy and quick methodology to generate SAPs. These gels were shown to absorb significant amounts of water and show great potential as functional materials in the superabsorbant industry.

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